EX-SITU SOIL WASHING OF DIESEL CONTAMINATED SOIL USING IMPINGING STREAM REACTORS AND SELECTIVE SOFT SELF ATTRITION

by

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Thesis submitted in partial fulfilment of the requirements for the degree of

Master of Science in Engineering (Chemical Engineering)

at the University of Stellenbosch.

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Stellenbosch December 1999

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DECLARATION

I, the undersigned, hereby declare that this thesis is my own original work, except where specifically acknowledged in the text. Neither the present dissertation nor any part thereof, has previously been submitted for a degree at any other university.

P. W. Maré

1 December 1999

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SYNOPSIS

When considering oil spills, the focus has usually been on the pollution of water and the corresponding impact on the animals and habitat concerned. There is, however, another important aspect that has largely been neglected - soil contamination. The remediation of diesel contaminated soil, making use of soil washing techniques consisting of two technologies i.e., Impinging Stream Reactors and Selective Soft Self Attrition was studied in this project. The primary aim of these processes will be as a pre-treatment step for bioremediation in a complete treatment system, capable of reducing total remediation times considerably.

The Impinging Stream Reactor (ISR) process uses a high pressure water jet to remove the diesel from the soil particles. The Selective Soft Self Attrition (SSSA) process uses a novel stirrer to stir a high density slurry (consisting of contaminated soil and water) resulting in interparticle scrubbing that removes the contaminant. Both processes were optimised with respect to all operating variables.

The most important variable in soil remediation is the particle size distribution to be treated. Four samples of silica sand differing only in particle size fraction were used to represent the range from fine silty soils (42% -10 μm) to coarse sandy soils (+500 μm). The Impinging Stream process was able to reduce diesel contamination levels in sandy soils by 96% (this corresponds to 2000 ppm, the most sensitive sites requiring levels below 200 ppm) but was not effective in treating silty soils. The Selective Soft Self Attrition process was able to reduce diesel contamination on sandy soils by 96% (to 2000 ppm) and silty soils by 94% (to 3000 ppm). Adding coarser sand as grinding agent to silty soils, reduces this value a further 2% (to below 2000 ppm).

Analyses of the sand (after washing) were done by extracting the diesel with Methylene Chloride in a Soxhlet Extraction Unit, after which the solvent was evaporated and the residual diesel determined gravimetrically. Altering the evaporation part by slowing it down considerably, resulted in improved accuracy and repeatability. Gas chromatographic analyses of the diesel extracted from the sand was also done and showed that the components in diesel lighter than C15 are being predominantly removed during these processes.

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SINOPSIS

Die fokus na 'n olieramp val gewoonlik op die aspekte van waterbesoedeling en die beskerming van die diere en habitat wat bedreig word. Daar is egter 'n ander belangrike aspek wat gewoonlik merendeels afgeskeep word - grondbesoedeling. Die remediasie van diesel besoedelde grond deur gebruik te maak van die twee tegnieke: Spuitreaktore en Selektiewe Sagte Self Attrisie is in hierdie projek bestudeer. Die hoofdoel van die twee tegnieke is om as vooraf behandeling vir bioremediasie te dien in 'n omvattende behandelings sisteem wat totale opruim tye sal verlaag.

Die spuitreaktor proses maak van 'n hoë druk water stroom gebruik om die diesel vanaf die grondpartikels te was. Die Selektiewe Sagte Self Attrisie proses gebruik 'n nuwe tipe roerder om 'n hoë digtheid flodder (bestaande uit die gekontamineerde grond en water) te roer wat 'n inter-partikel skuring veroorsaak en sodoende die kontaminant verwyder. Beide prosesse is geoptimiseer ten opsigte van alle bedryfsveranderlikes.

Die belangrikste veranderlike in grondremediasie is die partikel grootte verspreiding van die grond wat behandel moet word. Vier verskillende monters silika sand (wat slegs in partikel grootte verspreiding verskil) is gebruik om die spektrum vanaf fyn leemgrond (42% - 10 µm) tot growwe sanderige grond (+ 500 µm) te verteenwoordig. Die spuitreaktor proses het 96% van die diesel op die sanderige grond verwyder (dit stem ooreen met 2000 ppm, die mees sensitiewe areas benodig egter vlakke laer as 200 ppm), maar was nie suksesvol in die behandeling van leemgrond nie. Die Selektiewe Sagte Self Attrisie proses het 96% (2000 ppm oorblywend) van die diesel op die sanderige sand verwyder en 94% (3000 ppm oorblywend) van die diesel op die leemgrond. Deur growwe sand by die leemgrond te voeg is 'n verdere 2% diesel verwyder (2000 ppm oorblywend).

Analise van die sand (na die was proses) is uitgevoer deur die diesel met behulp van Metileen Chloried the ekstraheer in 'n Soxhlet Ekstraksie Eenheid waarna dié oplosmiddel afgedamp is en die oorblywende diesel gravimetries bepaal is. Deur die verdamping van die oplosmiddel te vertraag was dit moontlik om die akkuraatheid en herhaalbaarheid van die analises te verbeter. Gas chromatografiese analise, van die

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diesel wat geekstaheer is, het getoon dat componente ligter as C15 by voorkeur verwyder word gedurende die wasproses.

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ACKNOWLEDGEMENTS

The work presented in this dissertation was carried out in the Department of Chemical Engineering at the University of Stellenbosch, South Africa.

I would like to express my appreciation to:

- My Creator, without whom nothing is possible.
- My supervisor, Professor L. Lorenzen, for his guidance during this project.
- All the technical and workshop personnel, as well as Mrs. H. Botha for her valuable assistance with the analytical side of the project.
- My family who has stood by me through all my years of study.
- My friends and colleagues, who made the time spent here, an experience to remember.

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CHAPTER 1

INTRODUCTION

Imagine a world without oil. It is possibly the one natural resource that stands pivotal to modern civilisation. Spare a quick thought for the number of petroleum products and by-products the average man uses daily: petrol in the car, everything plastic… etc. Indeed oil is justly referred to as black gold.

Before the consumer can use this valuable resource, it has to be handled and transported repeatedly. The crude oil has to be taken from the oil field, refined and then sent to the respective industries where final products are made. One can just imagine the enormity of this if all the oil products and by-products are considered. This is exactly where the problem starts. Unfortunately we do not live in a perfect world and accidents happen. Spills occur at every place petroleum products are used and that includes gas station storage tanks, railroad yards, industries, harbours, airfields … etc.

Most oil spills we hear about, the focus is on the pollution of water and the impact on the animals and habitat concerned. However, considering the wide scope of spills already mentioned an important part has largely been neglected – soil contamination. Not only is it an eyesore, the soil is unsuitable for regular use, poses a threat to groundwater due to leaching and usually has to be removed from the spill site. Frequently this is done by excavating the contaminated soil and either encapsulating it or using it as landfill which incurs cost without actually accomplishing more than shifting the problem. Therefore, it is obvious that there is a big need for technology to be developed to effectively handle soil contamination.

The main objective set for remediation surely has to be to handle the problem as economically as possible. For the problem at hand, the target is to clean the soil sufficiently to adhere to legislation, so it can be returned to the site for future use without impacting the environment negatively. If possible, recovery of the valuable petroleum products for re-use as an energy source can aid in the cost effectiveness.

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Remediation of a contaminated site is achieved by one or more of the following paths:

- Removal or destruction of the contaminants,
- Modification of the contaminants to a less toxic, mobile or reactive form, and
- Isolation of the contaminant by interrupting the pathway of exposure.

A wide range of remediation methods are available to achieve above objectives from which two broad approaches can be distinguished:

- Engineering approaches: these primarily include the traditional methods of excavation and disposal to landfill or the use of appropriate containment systems.
- Process-based techniques: these include physical, biological, chemical, stabilisation/solidification and thermal processes.

Remediation technologies are also classified as either *in-situ* (unexcavated soil) or *ex-situ* (excavated soil) processes. Most remediation methods aim for rapid removal of the contaminant, making intensive use of energy and other resources. There is however, another approach called extensive treatment, which uses lower input methods and take longer to become effective but have lower cost and management requirements. Bioremediation being a good example.

Although individual unit processes may be suitable for treating a wide variety of contaminated soils, there are site-specific limitations, often related to either complex mixtures of contaminants or to the nature of the soil constituents, that may make the successful application of the techniques ineffective or uneconomic. Process integration is an approach where a combination of unit process treatments provide a more effective and economic overall treatment.

In this study, the focus will be on a particular physical process called soil washing. Two soil washing techniques will be examined as possible pre-treatment methods to be used and eventually in conjunction with bioremediation as a complete treatment system for contaminated soils.

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Soil washing is an ex-situ, water-based process that employs chemical and physical extraction and separation processes to transfer contaminants from the soil to the washing fluid. So, as the name implies, the soil is physically washed with water to remove the contaminant. A very simple and everyday analogy would be the washing of oily dishes (Couillard, Tran & Tyagi, 1991). The process transfers the oil to the water and can be enhanced by additions such as hot water and soap.

Of course, this washing can take various forms of which the application of the two technologies of impinging stream reactors and selective soft self-attrition will be studied in this thesis to determine their effectiveness and optimum operating conditions.

The essence of the method of impinging streams lies in the flow of two or more streams towards one another and the impingement at the midpoint of their flow, the so-called impingement plane. A highly turbulent region is formed and this is where intense washing and scrubbing will take place. The high-pressure water jet system is thus an ideal candidate to improve soil washing efficiencies thus far achieved. The jet reactor used was designed for gold leaching purposes and will be applied as is to this system.

SSSA is high intensity stirring of a high-density pulp using a new kind of stirrer. The stirrer blades are not solid, but instead comprise of a series of vertical stainless steel rods. This causes a movement of the particles in the pulp relative to one another producing intense scrubbing. The simplicity and increased scrubbing ability makes this technology attractive as a soil washing possibility.

Particle size is the major factor in soil washing. Using four samples of silica sand, only differing in size distribution, both techniques were evaluated over the entire range to be encountered and optimised with reference to the key operating variables.

Analyses of the soil samples are particularly problematic, and limitations and inaccuracies of commonly used methods are reported throughout the literature. By altering one of these methods slightly, the accuracy and repeatability of results were improved far beyond any of the methods encountered.

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CHAPTER 2

OVERVIEW OF SOIL CONTAMINATION AND REMEDIATION

The remediation of hydrocarbon contaminated soil covers a very broad and diverse field. One can just imagine the vast differences between the behaviours of sand and clay, the broad spectrum of hydrocarbon products in use today and the variety of technologies thusfar proposed to handle the ever-growing problem of pollution. In the following two chapters, the applicable literature will be discussed.

2.1 SOIL

Soil is the medium through which pollutants travel from the land surfaces to groundwater. Polluting substances are subjected to complex physical, chemical and biological transformations during their movement through the soil. Prediction of soil pollution and subsequent restoration, requires an understanding of the processes controlling the fate of pollutants in the soil medium and of the dynamics of the contaminants in the unsaturated zone (Yaron *et al.*, 1996).

Soil is the upper layer of the unsaturated zone of the earth. Soils are very diverse in composition as well as behaviour. The solid phase consists of mineral particles of various sizes and shapes and organic matter in various stages of degradation. Plant roots and the living soil population completes the eco-subsystem (Yaron *et al.*, 1996).

In nature, soils are heterogeneous assemblies of materials forming a porous media. The porosity of the soil system is controlled mainly by the association of its mineral and organic parts, with soil water also having a strong effect. This porosity can be affected by numerous processes, thus influencing the transport of pollutants to the groundwater. Figure 2.1 illustrates soil aggregation and soil porosity as affected by the soil components and the binding agents (Yaron *et al.*, 1996).

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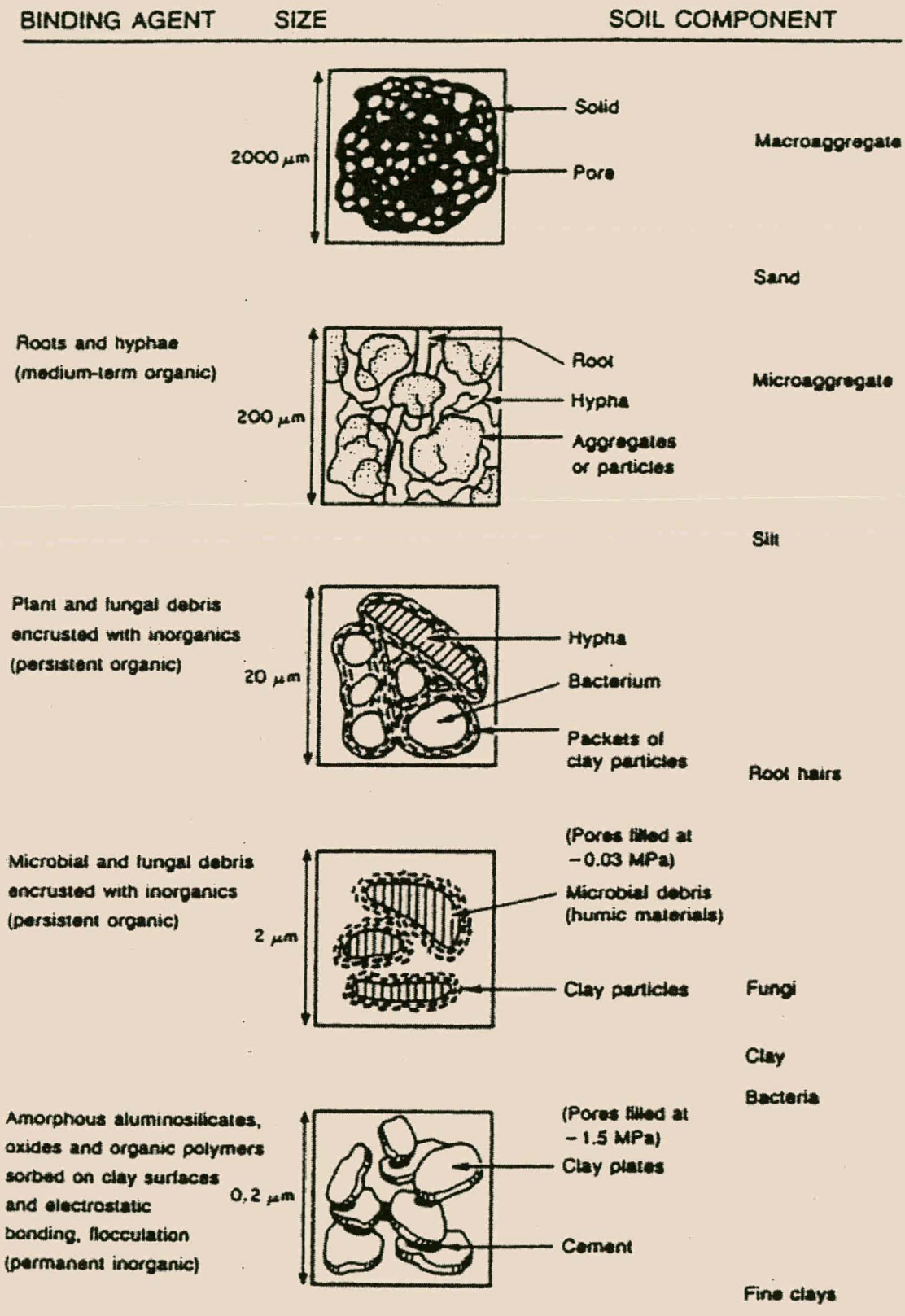

Figure 2.1. Model of a soil aggregate organisation (Yaron *et al.*, 1996).

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Table 2.1 gives a classification of soil pores.

Table 2.1. Functional classification of soil pores (Yaron *et al.*, 1996).

Name	Function	Equivalent cylindrical diameter [μm]
Transmission pores	Air movement and drainage of excess water	> 50
Storage pores	Retention of water against gravity and release to plant roots	0,5 – 50
Residual pores	Retention and diffusion of ions in solution	< 0,5
Bonding spaces	Support major forces between soil particles	< 0,005

When looking at possible interactions with various pollutants, the constituents of the soil solid phase should be grouped according to their surface area. The groups of constituents with low surface area mainly affect the transport of pollutants and those with high surface area control (besides transport) their retention and release to and from the soil surface. The fine clay and clay-organic complexes will thus be the most difficult to clean when polluted.

Clay is defined as the fraction of particles with a nominal diameter smaller than 2μm. The most common inorganic structural units to be found are the silica tetrahedron SiO_4^{4-} and the octahedral complex MX_6^{m-6b} (M being the metal and X some anions) (Yaron *et al.*, 1996).

The interactions among the various components of the solid phase of the soil strongly affect its surface activity. The mechanisms involved in adsorption of organic molecules on the mineral surface are shown in Table 2.2.

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Table 2.2. Mechanisms of adsorption for organic compounds in soil solutions (Yaron *et al.*, 1996).

Mechanism	**Principal organic functional groups involved**
Cation exchange	Amines, ring NH, heterocyclic N
Protonation	Amines, heterocyclic N, carbonyl, carboxilate,
Anion exchange	Carboxilate
Water bridging	Amino, carboxilate, carbonyl, alcoholic OH
Cation bridging	Carboxilate, amines, carbonyl, alcoholic OH
Ligand exchange	Carboxilate
Hydrogen bonding	Amines, carbonyl, carboxyl, phenylhydroxyl
Van der Waals interactions	Uncharged, nonpolar organic functional groups

The amount of water associated with the mineral surface greatly affects the adsorption of organic molecules by decreasing the number of active sites on the surface and sometimes affecting the adsorption mechanism itself (Yaron *et al.*, 1996).

Pollutants retained on and within the solid phase of the soil have reached the soil directly as solute, water-miscible liquid, suspended particles or in the gaseous phase. Pollutant retention is controlled by the physicochemical and physical properties of the soil solid phase, by the properties of the pollutants themselves and by environmental factors such as temperature and soil moisture content. Since under natural conditions we are dealing, in general, not with a single pollutant but a mixture of pollutants and natural organic and inorganic compounds, the competition for the soil adsorption sites will control their retention on or in the solid phase of the soil. For quantifying the retention of pollutants in the solid phase of the soil, an equilibrium should be determined. So major attention must be given to the kinetics of the process. The

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retention of pollutants on and in the solid phase of the soil are the result of a physicochemical process, adsorption on the surface, chemical reactions with the solid phase and mechanical trapping of the pollutants in the solid phase pores (Yaron *et al.*, 1996).

Adsorption is defined as the excess concentration of pollutants at the soil solid interface compared with that in the bulk solution or the gaseous phase, regardless of the nature of the interface region or of the interaction between the adsorbate and the solid surface which causes the excess. Surface adsorption is due to electrical charges and nonionized functional groups on mineral and organic constituents (Yaron *et al.*, 1996).

Adsorption of charged ionic pollutants on the surface of the soil solid phase is subject to a combination of chemical binding forces and the electric field at the interface that is implicitly controlled by adsorption itself. The soil solid phase has a net charge which, in contact with the liquid or gaseous phase, is faced by one or more layers of counter ions which have a net charge equal to and separated from the surface charge. Electrical neutrality on the colloidal surface requires that an equal amount of charge of the opposite sign must accumulate in the liquid phase near the charged surface.

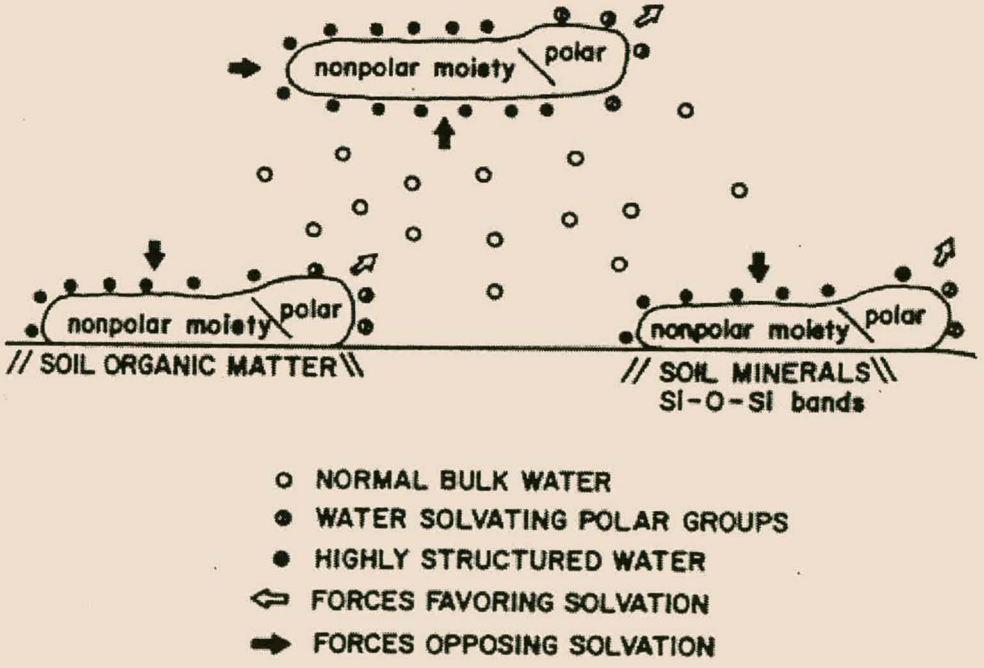

Figure 2.2. Diagrammatic model of forces contributing to the sorption of nonpolar (hydrophobic) organics (Yaron *et al.*, 1996).

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The adsorption of nonionic pollutants on the solid phase surfaces of the soil is subjected to a series of mechanisms such as protonation, waterbridging, cation bridging and van der Waals interactions. This class of pollutants includes chlorinated hydrocarbons, organophosphates, anilines, etc.

Chemical adsorption means simplistically that the chemical has become associated or attached to the solid phase and removed from the liquid phase or gaseous phase. It is of course a lot more complex and includes processes such as ion exchange, surface complexation, inner and outer sphere complexation and fixation. Adsorption is a surface and interfacial process occurring at the interface between solid and liquid/gaseous phases. The adsorbed ions or molecules have neither completely joined the solid phase nor been completely removed from the liquid phase. The adsorption capabilities of the soil come from the presence of functional groups located at the surface of soil particles. Some of these functional groups exhibit a charge, which attracts oppositely charged ions in the solution. Some functional groups in the soil are uncharged and play a role in the bonding of neutral molecules. The stereochemical properties of the surface functional groups, the degree to which the surface charge is localised or dispersed, the solution ionic strength and the hydrated radii of the sorbing ion, all affect how and where adsorption will occur. The presence of charged adsorption sites is one of the most well known properties of soil. Charged adsorption sites (or exchange sites) are classified as permanent or pH dependant. Permanent charge comes from isomorphic substitution of atoms in the crystal lattice of layer silicate clay minerals. A negative charge gives rise to the cation exchange capacity (CEC) of soils. Isomorphic substitution (permanent charge) is a process essentially limited to clay minerals (particles $< 2\mu m$). Adsorption is generally a competitive process where ions compete for adsorption sites. Increased site affinity can be the result of stereochemical geometries, greater charge or the ability to form a molecular complex with a surface functional group. Some general conclusions regarding adsorption are that a higher charge implies higher affinity to exchange sites, organic molecules tend to absorb or partition to soil organic matter or uncharged sesquioxide surfaces and anions sorb primarily to soil organic matter or sesquioxide surfaces.

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While adsorption is positive in that it inhibits spread of pollution, the same properties create the soil-washing problems (Jones & Ghassemi., 1994).

Theoretically, the adsorption-desorption process should be expressed by isotherm singularity. Unfortunately, this is not the case in the real world and the phenomenon of hysteresis is all too often encountered. Here a certain amount of the contaminant cannot be released or at best is released very slowly over a long period of time. The nature of the solid phase, the specific pollutant, experimental conditions, soil history and environmental conditions as well as the presence of biological agents, all affect the bonding to the soil. Retention hysteresis is not yet fully understood, but the fact remains that certain conditions create an environment where the pollutants become permanently part of the soil. Two major categories have been identified: molecules that are retained through physical interactions and are able to be desorbed (for instance trapping) and molecules that have evolved such that they interact strongly with the solid matrix and are thus released slowly or not at all. This retention is a result of either physicochemical processes or biological processes. Physicochemical retention involves adsorption followed by a chemical reaction with the surface where the pollutant becomes tightly bound or even chemically altered. Biological processes involve a degradation of the species thus altering its properties (Yaron *et al.*, 1996).

It was decided that silica sand would be used due to its abundance and inertness. After oxygen, silicon is the most abundant element on earth (Ryan, 1968), so using silica sand will be very representative of real soil compositions. Inertness guarantees that the washing processes can be studied without any undesirable reactions (between the contaminant, washing fluid and soil) influencing the results. Four samples of sand varying only in particle size distribution were used to represent the real situation. The sand was bought from Consol Glass in Cape Town.

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Table 2.3. Sand used in this study.

	Industry Name	Average Particle Size	New Name (to be use further in thesis)
1.	No. 1 Foundry sand	0.51 mm	500 μm
2.	AFS 35 Foundry sand	0.35 mm	300 μm
3.	No. 2 Foundry sand	0.12 mm	100 μm
4.	Silica 300 mesh	0.01 mm	10 μm

Original data sheets containing the composition and size distribution of each sample of sand can be found in Appendix C.

2.2 HYDROCARBON CONTAMINANT

A contaminant can be defined as a substance that, when present in sufficient quantities or concentrations, are likely to be harmful (directly or indirectly) to humans or the environment (Martin & Bardos, 1994). This study will focus on the hydrocarbon contaminant, diesel.

Petroleum oil is generally considered to be formed from animal and vegetables debris accumulating in sea basins or estuaries and buried there by sand and silt. The debris may have been decomposed by anaerobic bacteria under reducing conditions, so that most of the oxygen has been removed, or oil may have been distilled from the partially decayed debris by heat generated from earth movements or by depth of burial. The final result is a black viscous product of composition (Francis, 1965):

Table 2.4. Composition of oil.

Carbon	80 to 89 %
Hydrogen	12 to 14 %
Nitrogen	0,3 to 1 %
Sulphur	0,3 to 3 %
Oxygen	2 to 3 %

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Temperature changes, earth movements, and differences in density between oil and salt water caused the oil to migrate from the source rock to accumulate in favourable geological formations. Favourable locations mean a porous sedimentary rock, called a 'reservoir rock' in which oil and gas can accumulate in the upper layers, capped by an impermeable rock, or rock formation, which prevents escape of the oil and gas. These oil fields are located and drilled to produce the crude oil.

Crude oils are commonly classified into the following three main groups, depending upon the type of hydrocarbons that predominate in the oil: (1) Parrafinic, (2) Naphtenic and (3) Asphaltic (aromatic). Crudes contain a wide variety of hydrocarbons, ranging from the simplest hydrocarbon gas, methane, to the most complex solid paraffin wax or bitumen (Francis, 1965).

Crude oil from a well contains impurities such as water, solids (including sand, bitumen or wax) and gas (mainly methane and ethane). These impurities separate partially in storage tanks. The crude oil then has to be distilled on site, or sent to refineries for distillation and further processing before the resulting products are suitable for use (Francis, 1965). Refineries are designed to produce 'fractions', or batches of different hydrocarbons boiling within certain predetermined ranges of temperature. Figure 2.3 shows the fractional distillation distribution of crude and refined oils (Yaron *et al.*, 1996).

Apart from petroleum, there are three other sources of crude oil: (1) coal liquefaction, (2) shale oil and (3) tar sands. Coal must be treated to increase it's hydrogen content and remove undesirable elements such as nitrogen, sulphur, arsenic, mercury, cadmium and phosphorous. Shale oil is difficult to get out of the ground since it is soaked up in rocks. Tar sands contain hydrocarbons mixed with sand and are difficult to remove from the ground. Like coal derivatives and shale oil, oils from tar sands require hydrogenation and removal of undesirable chemicals from the crude before it is delivered to the refinery. The same kind of distillation is then employed to physically separate the crude into fractions as mentioned earlier (Ferguson, 1986).

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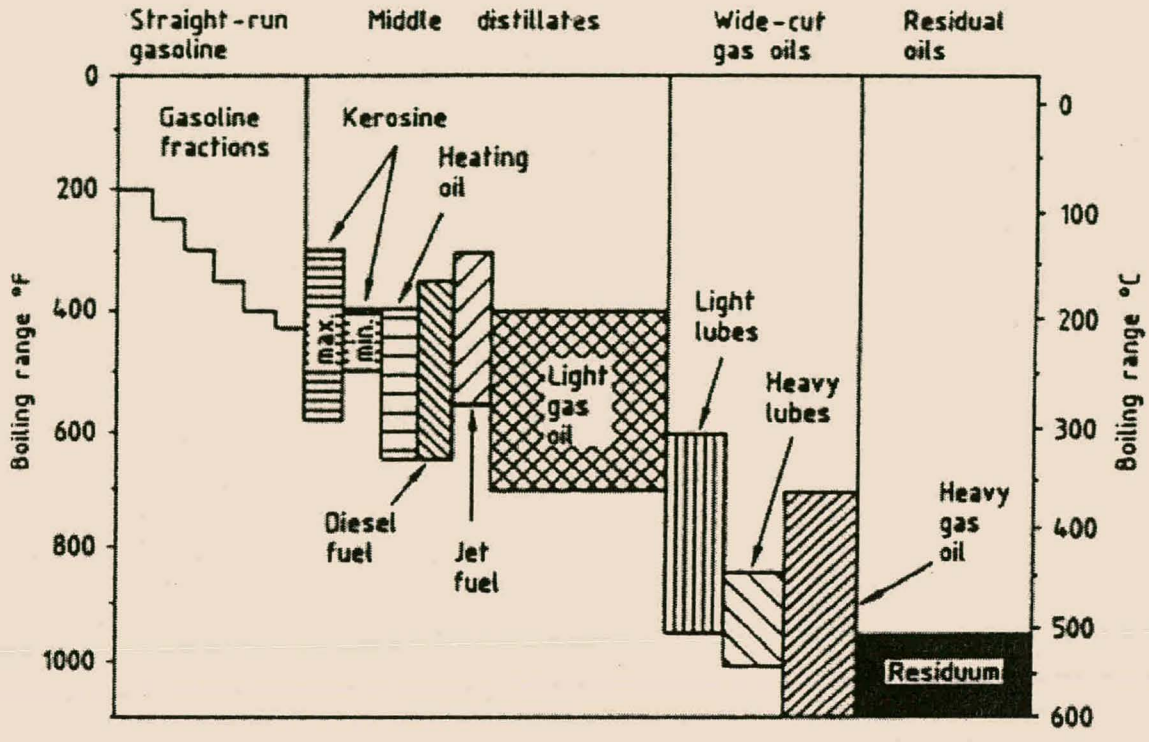

Figure 2.3. Fractional distillation distribution of crude and refined oil (Yaron *et al.*, 1996).

In this study, diesel fuel will be used to represent the hydrocarbon contaminant group due to its wide spread use and representative range of species and to evaluate the effectiveness of the remediation technologies proposed. Figure 2.3 shows that diesel is a middle distillate with a boiling point ranging between 170°C – 340°C. Due to the way the diesel is produced, all lighter weight hydrocarbons (C1 to C8) and most of the volatile aromatic compounds such as benzene, toluene, xylene, and ethylbenzene are removed. Most of the polynuclear aromatic compounds have a higher boiling point and are eliminated. Only the lighter molecular weight polynuclear aromatics (naphthalene, 2-methylnaphthalene and phenanthrene) and the volatile aromatics with lower vapour pressures such as toluene, are present in diesel in varying concentrations.

Figure 2.4 shows a typical chromatograph of diesel with the major species identified.

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Hydrocarbons C_{10} - C_{28} Application 199 - GC

The analysis of Diesel oil

Technique	: GC - capillary
Column	: 25 m × 0.32 mm fused silica WCOT CP-Sil 5 CB (0.12 µm) (Cat.no. 7740)
Temperature	: 80°C (1 min) → 320°C, 10°C/min
Carrier gas	: He, 80 kPa (0.8 bar, 12 psi), 53 cm/s
Injector	: Splitter, 180 ml/min T = 250°C
Detector	: FID, 256 × 10^{-12} A/s T = 310°C
Sample size	: 0.5 µl
Solvent sample	: n-hexane, sample 1 : 1 diluted

Peak identification :

1. C_{10}
2. C_{11}
3. C_{12}
4. C_{13}
5. C_{14}
6. C_{15}
7. C_{16}
8. C_{17}
9. pristane
10. C_{18}
11. phytane
12. C_{19}
13. C_{20}
14. C_{21}
15. C_{22}
16. C_{23}
17. C_{24}
18. C_{25}
19. C_{26}
20. C_{27}
21. C_{28}

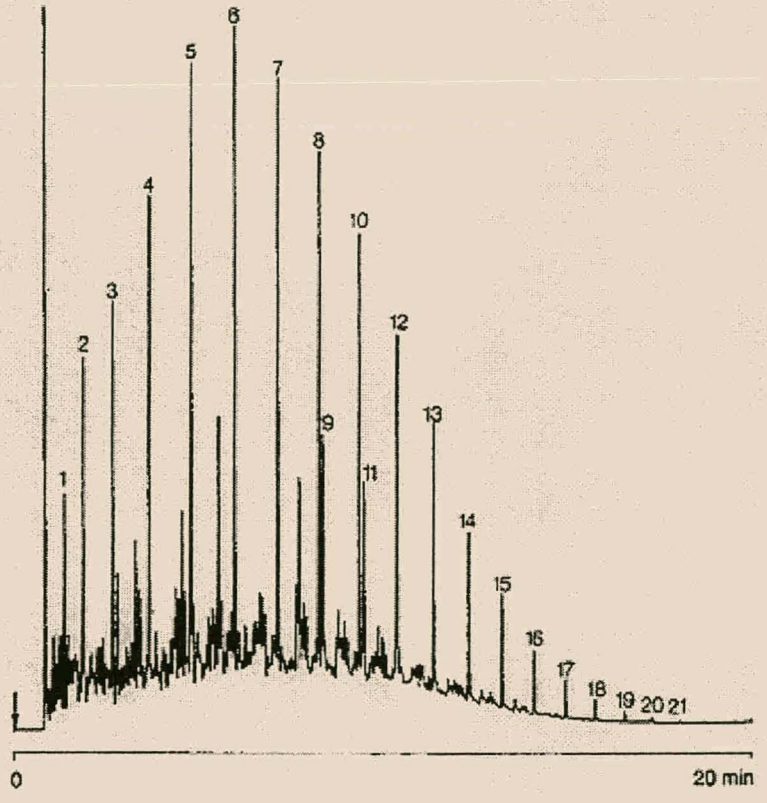

Figure 2.4. Major components of diesel

The major components of diesel is shown in Table 2.5. Due to the variability of crude even on the same oil field, the proportions of the major classes may vary slightly.

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Table 2.5. Detailed analyses of diesel (Demque, et. al., 1997).

Hydrocarbon type	Percentage volume [%]
Paraffins (n- and iso-)	41.3
Monocycloparaffins	22.1
Bicycloparaffins	9.6
Tricycloparaffins	2.3
Total saturated hydrocarbons	75.3
Olefins	-
Alkyl benzenes	5.9
Indans/Tetralins	4.1
Dinapthtenobenzenes	1.8
Naphtalenes	8.2
Biphenyls/acenaphthenes	2.6
Fluorenes/acenaphthylenes	1.4
Phenanthrenes	0.7
Total aromatic hydrocarbons	24.7

2.3 ALTERNATIVE SOIL REMEDIATION TECHNOLOGIES

As mentioned previously the soil remediation technology to be used in this study is the physical process of soil washing using two unit processes namely, impinging stream reactors and selective soft self-attrition. Of course there are numerous other processes available and to put the merit and results of this study into perspective, one needs to evaluate all these technologies, their areas of applicability and the successes obtained with them. A brief description of available related technologies are described below.

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2.3.1 Removal to Landfill

Landfill involves the three stages of soil excavation, transport to and burial at the landfill site. This approach represents a rapid method of dealing with almost any contaminated site, but it has been criticised as it represents only a transfer of the contaminated material from one location to another rather than a final solution. It has been used excessively in the past partly because other options were not available or proven viable yet. Landfills are designed to ensure that contaminants are either isolated from the environment or subjected to attenuation processes so that they no longer cause harm to the environment. Relatively low landfill disposal costs are the major incentive for this type of disposal, although some recent increases in the cost of disposal of hazardous material to landfill may result in some reduction in this approach, especially when large volumes are considered.

Contaminated material disposed off to landfill must be prevented from causing any further environmental damage. The principal approaches that contribute towards prevention are containment and attenuation. Containment measures are designed to isolate the disposed material from the environment such that any liquid or gaseous interchange is minimised or controlled. The effective design and installation of a containment system requires extensive geological and hydrological investigation, modelling and monitoring. This isolation may be achieved by a range of techniques, including lining, capping, cover systems and sometimes, vertical barriers (Wood, 1997).

Any materials used for containment may also act as a substrate for attenuation mechanisms. Attenuation occurs as a result of various mechanisms operating in the landfill, which serve to minimise the movement and/or reduce the toxicity of contaminants. Attenuation mechanisms can be physical, chemical or biological. Physical methods include the adsorption and absorption of contaminants, filtration dilution and dispersion. Chemical methods of attenuation include acid-base interactions, oxidation, reduction, precipitation and ion-exchange. Biological methods of attenuation include aerobic and anaerobic microbial degradation. Most of these mechanisms require the presence of organic material within the landfill and so co-

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dispersal operations are favourable as these include the disposal of decomposing municipal waste (Wood, 1997).

Looking at diesel contaminated sand, this technology off course does not reduce the contamination levels and as stated earlier only transfers the problem somewhere else. Cost of disposal will play the major part when considering alternatives.

2.3.2 On-Site Containment

An alternative to removal to a landfill can be containment of the excavated contaminated material on-site. Containment measures are designed to prevent or limit the migration of contaminants, or any associated leachate or gaseous products, to the wider environment (leachate or gas collection systems can also be used). Approaches include hydraulic measures, capping, use of break layers and low permeability barriers amongst others. The barriers can be constructed from natural or synthetic materials, or a combination of both, and can be placed over, under or around a contained area or pollution source. The technique can be used to isolate existing hazards or prevent the spread of contaminants from disposal sites. Landfills receiving controlled wastes usually incorporate containment systems (Wood, 1997).

A cover system consists of a single layer, or succession of layers, of selected non-contaminated material that covers the area of contamination. The cover system should prevent exposure to the harmful substances, sustain growth of vegetation and control infiltration to and from the site. The type of material to be used depends on the physical properties required by any particular component layer and possible materials are:

- Natural clays, sub-soils and soils.
- Amended soils incorporating pulverised fuel ash, lime and sludge.
- Waste materials like fly-ash, slags, dredgings, sewage sludge.
- Synthetic membranes and geotextiles.
- Concrete and asphalt.

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Although covering the contaminated surface with a clean material incorporating a low permeability layer reduces infiltration and forms a physical barrier to the contamination, it may not adequately control the movement of contaminants and allow the ingress and egress of water and contaminants in all directions. Neither do they control the groundwater movements, gaseous emissions and odours so that long term monitoring may be necessary. In order to provide adequate control it may be necessary to use such cover systems in conjunction with vertical and horizontal in-ground barriers or cut-offs to achieve partial or total isolation of the site (Wood, 1997).

In-ground barriers can be used to isolate, usually by physical means, a contaminated mass of ground from the surrounding environment or other targets. Low permeability material may be introduced around or under the contaminated site, or methods incorporating some sort of physical, biological or chemical control of contaminant migration can be used. Vertical barriers are constructed by excavation, displacement or injection. In practice, it is often difficult to ensure continuity of the barriers. This technology again does not offer a final solution, for the problem will just have to be handled at a later stage when the barriers eventually fail (Wood, 1997).

For the diesel-contaminated sand, this technology also does not reduce the contamination levels and once again the costs to be incurred will be the deciding factor. The ground above the contained area could however, be used and this should be kept in mind.

2.3.3 Road Base and Asphalt Batching

This option is very cost effective where the contaminated soil is close to an area of active road construction. The contaminated soil is spread in the proposed roadway, compacted, and oiled according to standard construction protocol. The contaminated soil is no different from uncontaminated soil under the same road. When a high percentage of expandable clays are present in the soil it may not be suitable for this option.

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A related use is where the diesel-contaminated soil replaces part of the sand and gravel component of asphalt and as high as 5% has been used (Dineen, 1991).

2.3.4 Stabilisation/Solidification

Stabilisation/Solidification processes involve solidifying contaminated materials, converting contaminants into less mobile chemical forms and/or binding them within an insoluble matrix, presenting a minimal surface area to leaching agents (Wood, 1997). The contaminant is encapsulated in a monolithic solid of high structural integrity. It is when the process results in chemical fixation of contaminating substances that the term stabilisation can be applied (Martin & Bardos, 1994).

These processes can be used to treat soils, wastes, sludges, liquids and a number of contaminant types. Many of the reagents used however, are exclusive to specific contaminants. An added benefit though is the improved handling and geotechnical properties of the treated product, compared to the original contaminated material. The treatment of organic contaminants is generally more difficult and more expensive (Wood, 1997).

Stabilisation/solidification processes have been applied both in-situ and ex-situ. With an ex-situ approach, the ideal is to find an alternative use for the end product. If none can be found the disadvantage is now to landfill a considerably greater volume of the stabilised product than the original contaminated material because of the quantities of stabilisation material added (Wood, 1997).

Processes can be classified according to the type of material used as binder. The more frequently applied methods use: Portland cement, pozzolonic materials such as fly ash, lime, silicates, clays (often used in conjunction with other materials) and polymers (Wood, 1997; van Zyl, 1997; Alberts, 1996). Much research is still possible in the field that can result in long term solutions to some specific contaminant problems.

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With these processes, the contaminant is contained rather than destroyed or detoxified and there are uncertainties over long-term performance, especially with organic contaminants (diesel in this case). This technology is also fairly expensive.

2.3.5 Thermal Processes

Thermal processes use elevated temperatures (800 – 2500 °C) to remove or destroy toxic contaminants by inducing physical and chemical processes, such as incineration, gasification, combustion, desorption, volatilisation, pyrolysis or some combination of the above mentioned. Although thermal processes have been around for a number of years, new methods are being developed continuously to provide cost-effective solutions. The majority of thermal processes are applied to excavated soil although a number of in-situ methods exist (Wood, 1997). Thermal systems can treat almost any type of contaminated soil, although soils with high contents of clays and moisture require higher energy input and are difficult to handle (Martin & Bardos, 1994).

Using three ex-situ techniques, thermal desorption, incineration and vitrification, operation in three different temperature regimes will be discussed. In thermal desorption, the excavated soil is heated to around 600 °C where all the volatile contaminants are evaporated and removed by condensation, scrubbing, filtration or destruction at higher temperatures. This is primarily used for toxic organic contaminants but has also been used for mercury contaminated soils (the mercury has to be condensed downstream of the process) (Wood, 1997).

Incineration operates between 880 °C and 1200 °C and results in destruction of the soil texture and removal of all natural humic components. The contaminants are destroyed or detoxified (exhaust gases need to be treated) and residues may have a high heavy metal content. Rotary kilns are mostly used and the technique can also be used for contaminated liquids and sludges (Wood, 1997).

Vitrification takes place at 1000 °C to 1700 °C and a monolithic solid glassy product (melted aluminosilicate minerals) is formed. Contaminants are either destroyed or

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trapped in this glassy product. The process is very expensive, has a low leaching capacity and will only be used for very harmful substances (Wood, 1997).

Thermal treatment of diesel contaminated soil uses high temperatures to oxidise diesel to carbon dioxide and water. This can occur in cement kilns, where the diesel provides fuel for heating the kiln and the soil is incorporated into the cement mixture, or in specially designed thermal units that bake the soil to drive off the diesel and subsequently oxidise it. Heated air or steam can also be used to raise the temperature in the soil to drive off the diesel. When using in-situ steam extraction there has to be a groundwater collection system because the steam condenses in the soil and leaches to the groundwater. A hazardous waste incinerator can also be used to burn diesel in the soil, but this is very expensive and far more intensive than generally required. Total removal may thus be possible with thermal processes but this technology is rather expensive (Dineen, 1991).

2.3.6 Chemical Processes

Chemical treatment processes are designed either to destroy contaminants or to convert them to less environmentally hazardous forms. Chemical reagents are added to the soil to bring about the desired reaction. In general, excess reagents may need to be added to ensure that the treatment is complete. This in turn may result in excessive quantities of unreacted reagents remaining in the soil. Heat and mixing may also be necessary to support the chemical reaction. Chemical processes can also concentrate contaminants in a manner similar to physical processes. Most processes have been developed for groundwater clean up. The major types widely used at full scale are; oxidation-reduction, dechlorination, extraction, hydrolysis and pH adjustment (Wood, 1997).

Chemical processes can be applied either in-situ or ex-situ. Processes have been developed ex-situ for the remediation of organic and inorganic contaminants by oxidation or reduction to a more stable, immobile and less toxic form. Examples include the reduction of Chromium (VI) to Chromium (III) using ferrous ammonium sulphate and the reductive dechlorination of halogenated organic compounds.

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Chemical extraction processes can be used to transfer the contaminant from the soil to a leachate, which can be collected, concentrated and treated. This approach can be used to deal with both organic and inorganic contaminants, using extraction agents such as organic solvents, acids and alkali's, surfactants, and supercritical fluids. Successful extraction requires conditions of intimate mixing between the soil and the liquid. *In situ* extraction methods, referred to as soil flushing, have been operated in the field. *In situ* extraction processes, such as the physical excavation and cleaning of contaminated groundwater (called pump and treat), are often classified as physical processes (see below) but are included here since chemical reagents can be added to the flushing solution (Martin & Bardos, 1994). Many processes in other categories may also use chemical processes for the treatment of effluents and gaseous emissions.

By using a strong oxidant, usually hydrogen peroxide, diesel is oxidised to carbon dioxide and water (Dineen, 1991). It is possible to achieve complete removal but the costs of chemicals will play a big role when considering this alternative.

2.3.7 Bioremediation

Bioremediation is defined as the manipulation of living systems to bring about desired chemical and physical changes in a confined and regulated environment (Cacciatore & Mc Neil, 1995). The objective is the degradation of contaminants to harmless intermediates and end products, and ultimately the complete mineralisation of contaminants to carbon dioxide, water and simple inorganic compounds (Wood, 1997).

For millions of years, micro-organisms have performed this function, using natural physiological processes of recycling dead organic matter from which new plant life could grow. Micro-organisms such as bacteria, fungi and yeast are now used to dissolve and/or degrade complex organic contaminants, such as petroleum hydrocarbons in the soil and water, into simpler organic molecules and eventually into carbon dioxide and water.

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These organisms have enzymes that can degrade naturally occurring compounds. Contaminated soils however, normally contain man-made organics that are more difficult to degrade. The microbial enzyme system of the organisms must first acclimatise to these manmade chemicals before degradation can occur, after which the biodegradation rate increases along with the production of new micro-organisms. When micro-organisms come into contact with complex organic materials, extracellular enzymes are released to convert high molecular weight materials into diffusable fractions, which could be transported through the cell wall for assimilation. The molecular structure of a pollutant is irreversibly altered by this biological action such that basic physical and chemical properties are lost (Van Zyl, 1998).

It is well established that the lower molecular weight compounds are readily degraded by micro-organisms. The heavier molecular weight compounds are more resistant to degradation, especially when adsorbed onto the soil. However, even the heavier molecular weight compounds will degrade given sufficient time (Demque *et al.*, 1997).

For a microbial population to thrive they not only require a source of nourishment (in this case the petroleum hydrocarbons) but also specific macronutrients (nitrogen, phosphorous and potassium), a terminal electron acceptor (oxygen in aerobic systems), an aqueous environment (a function of the soil moisture content) and an acceptable temperature regime (Demque *et al.*, 1997). These requirements are usually met through adding fertiliser, tillage and irrigation. Thus, we are basically just trying to make the best use of what nature has provided.

Bioremediation can be done both in-situ and ex-situ (also aerobic and anaerobic). Ex-situ methods include traditional approaches such as land farming and composting, and more recent developments such as using aerobic or anaerobic bioslurry reactors (for the treatment of organic contaminants in clays and silts) and can be done static or dynamic. Static ex-situ methods entails leaving the excavated soil undisturbed for the duration of the treatment; conditions can be monitored and water, air and nutrients added if required (e.g. biopiles, composting). Dynamic ex-situ processes requires, in addition to water, air and nutrients, dynamically mixing the soil to encourage rapid degradation (e.g. landfarming, windrow turning, bioreactors). Runoff and leachate are

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controlled. In-situ methods include pump and treat systems where the natural biodegradation process is enhanced and controlled by the supply of oxygen and nutrients to the underground contaminated mass (Martin & Bardos, 1994; Wood, 1997; Dineen, 1991)

Bioremediation is an attractive option being a natural process and releasing harmless products into the environment. There is considerable scope for integration with other remediation processes, either as pre-treatment to increase the availability of contaminants to other processes or as final treatment, to remove the last traces. From a cost point of view, it is also very beneficial as well as being less disruptive to the environment (when in-situ methods are used) than processes requiring excavation. The only serious drawbacks seems to be the time required for remediation, rendering this technology unsuitable for emergency cleanups, the area of land required for the operation (ex-situ) and the potential for volatilisation of harmful organics (sometimes intermediates) into the atmosphere (Demque *et al.*, 1997; Wood, 1997).

Bioremediation of diesel contaminated soil is the most widely applicable alternative to landfill disposal and cleanup levels lower than 100 ppm can be achieved. Diesel hydrocarbons are degraded into harmless alchohols, ketones and organic acids, all of which ultimately degrade to carbon dioxide and water.

2.3.8 Physical Processes

Physical processes separate contaminants from uncontaminated material by exploiting differences in their physical properties (e.g. density, particle size, volatility) by applying some external force (e.g. abrasion) or by altering some physical characteristic to enable separation to occur (e.g. flotation). Depending on the nature and distribution of the contamination within the soil, physical processes may result in the segregation of differentially contaminated fractions (for example, a relatively uncontaminated material and a contaminant concentrate based on a size separation) or separation of the contaminants (for example, oil and metal particles) from the soil particles (Wood, 1997).

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The range of physical processes includes both in-situ and ex-situ methods. This variation can be classified into two main groups: washing and sorting treatments, and extraction treatments. The main aim of washing and sorting treatments is to concentrate the contaminants into a relatively small volume so that the cost associated with disposal and further treatment are related only to the reduced volume of process residues. Washing treatments transfers the contaminant from particle surfaces into an aqueous phase (sometimes using chemical additives), where this contaminant-rich liquor can then be treated as wastewater. Sorting treatments separate from the soil those particles containing the contaminants by mineral processing techniques or exploiting differences in the properties of individual soil particles (Wood, 1997).

Extraction treatments involve processes that remove the contaminants from the soil matrix by involving a mobilising and/or releasing process. Soil vapour extraction is an *in situ* process where a vacuum is applied through extractions wells to create a pressure gradient that induces gas phase volatile contaminants to flow through the soil to the extraction wells, where they are then removed from the soil. Electroremediation is an *in situ* process where an electrical current is passed through an array of electrodes that is embedded in the soil. When the current is applied, movement of contaminants in the pore water towards the electrodes is induced by electrolysis, electro-osmosis and electrophoresis. The electrodes have porous housing into which purging solutions are pumped to remove the contaminants and bring them to the surface. The purging solutions are then pumped to a water treatment plant for contaminant removal. Soil flushing and chemical extraction are processes that use chemical reagents, solutions or steam to mobilise and extract contaminants form soils. Mobilisation refers to the release of dissolved contaminant ion from sorbed or precipitated forms in soils and may form part of both *in situ* soil flushing and *ex situ* chemical extraction treatments (Wood, 1997).

The range of methods available here are very wide and well suited to handle diesel contaminated soil especially as a pre-treatment method to produce a clean large fraction and a reduced volume of soil (fine fraction) that can be treated by more expensive methods.

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This study focuses on a particular physical process called soil washing. The next chapter is dedicated to discussing this technology and finally the two processes used; Impinging Stream Reactors and Selective Soft Self Attrition.

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CHAPTER 3

LITERATURE REVIEW

3.1 SOIL WASHING

Soil washing is an ex-situ, water-based process that employs chemical and physical extraction as well as separation processes to remove organic, inorganic, and radioactive contaminants from soil. It is usually employed as a pre-treatment process in the reduction of the volume of feedstock for other remediation processes thereby reducing overall costs (Anderson, 1993).

3.1.1 Process Description

Figure 3.1 shows a general schematic of the soil washing process.

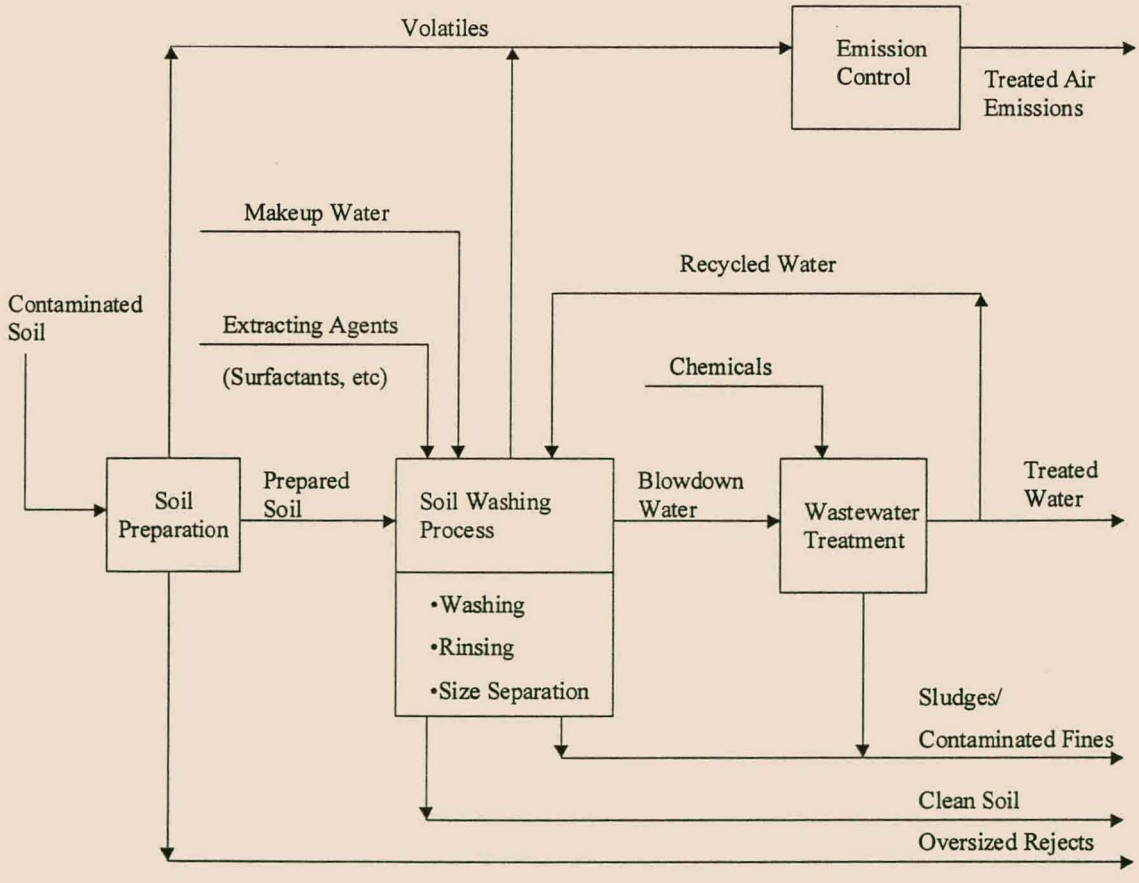

Figure 3.1. Aqueous soil washing process (Boulding 1996).

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As seen on the diagram, the soil is prepared first by excavation and mechanical screening to remove oversized material and debris. The soil is then mixed with washwater and possibly extraction agents to remove the contaminant from the soil. The process removes contaminants from soils in one of two ways: by dissolving or suspending them in the wash solution (which is later treated by conventional waste water treatment methods) or by concentrating them into a smaller volume of soil through particle size separation techniques. The concept of reducing soil contamination using particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either physically or chemically, to clay and silt particles. The clay and silt particles are in turn attached to sand and gravel particles by physical processes such as compaction and adhesion and are separated during washing (Boulding, 1996).

The soil and washwater is separated and the soil rinsed with clean water. The process recovers a clean soil fraction (coarse fraction, sands and gravel) and concentrates the contaminants in another soil portion (fine fraction, silts and clays) and the washwater. The clean soil fraction is returned to site and the washwater and fine fraction is treated further (Boulding, 1996).

Soil washing performance is highly sensitive to site conditions. The process is most effective when applied to soils and sediments containing large proportions of sand and gravel and is relatively ineffective when applied to soils having a high silt and clay content (Anderson, 1993).

3.1.2 Applications

The potential applications of soil washing include; petroleum and fuel residues, organic solvents, radionuclides, heavy metals, polychlorinated biphenyl's (PCB's), wood preserving chemicals (pentachlorophenol (PCP), creosote), pesticides, cyanides, semivolatiles and volatiles (Anderson, 1993). Volatile organic contaminants are often easily removed with efficiencies of 90 – 99%. Semivolatile organics are removed to a lesser extent, 40 – 90%, by selection of a proper surfactant. Metals and pesticides, which are insoluble in water, often require acids or chelating agents to achieve good

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results (Boulding, 1996). The effectiveness of soil washing for general contaminant groups is shown in Table 3.1.

Table 3.1. Applicability of soil washing on general contaminant groups for various soils (Boulding, 1996).

Contaminants Groups	Sandy/Gravelly Soils	Silty/Clay Soils
Organic		
Halogenated volatiles	□	∇
Halogenated semivolatiles	∇	∇
Nonhalogenated volatiles	∇	∇
Nonhalogenated semivolatiles	∇	∇
PCB's	∇	∇
Pesticides (halogenated)	∇	∇
Dioxans/furans	∇	∇
Organic cyanides	∇	∇
Organic corrosives	∇	∇
Inorganic		
Volatile metals	□	∇
Nonvolatile metals	□	∇
Asbestos	O	O
Radioactive materials	∇	∇
Inorganic corrosives	∇	∇
Inorganic cyanides	∇	∇
Reactive		
Oxidisers	∇	∇
Reducers	∇	∇

□ Good to excellent applicability: High probability that technology will be successful.

∇ Moderate to marginal applicability: Exercise care in choosing technology.

O Not applicable: Expert opinion that technology will not work.

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As mentioned previously soil washing is most appropriate for treating non-complex soils that contain at least 50% sand and gravel, such as, coastal sandy soils and soils with glacial deposits and is relatively ineffective in treating soils that are rich in clay and silt sized particles (Anderson, 1993). Particle size distribution is the key physical parameter for determining the efficiency of a soil washing process and should be used as a preliminary screening measure. Figure 3.2 shows this simplistically as curves over the whole range of particle sizes (Boulding, 1996).

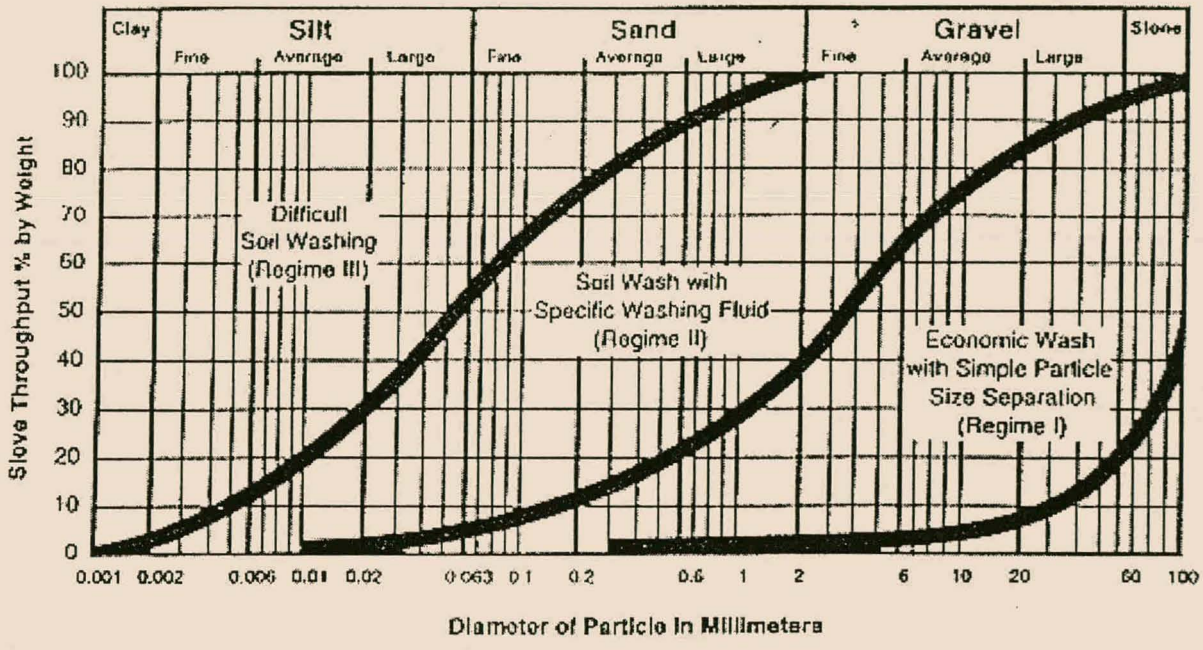

Figure 3.2. Soil washing applicable particle size range (Boulding, 1996).

Further, soils with a relatively high cation exchange capacity (the capacity to exchange cations for those in the polluting substance) tend to bind pollutants more tightly. Site characterisation is the first and most important step in determining whether soil washing may be effectively applied. Removal efficiencies are highly dependent on a specific physical and chemical characteristics of the soil and the contaminants and on the spatial distribution of pollutants throughout the soil. Among the extensive data required for site characterisation are the site geology and hydrogeology, soil type and composition versus depth, soil chemistry, and variability of contaminants in the soil. It is important to know how soil type and contaminant concentrations change with latitude and depth in order to develop an accurate profile of the feedstock soil and to guide sampling efforts in collecting representative soils

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for further characterisation and for bench and pilot testing (Anderson, 1993). Table 3.2 shows the physical and chemical characterisation parameters of the soil to be considered.

Table 3.2. Waste soil characterisation parameters (Boulding, 1996).

Parameter	Purpose and Comment
Key Physical	
Particle size distribution:	
> 2mm	Oversize pre-treatment requirements
0.25 – 2 mm	Effective soil washing
0.063 – 0.25 mm	Limited soil washing
< 0.063 mm	Clay and silt fraction – difficult soil washing
Other physical	
Type, physical form, handling properties	Affects pre-treatment and transfer requirements
Moisture content	Affects pre-treatment and transfer requirements
Key chemical	
Organics	
Concentration	
Volatility	
Partition coefficient	Determine contaminants and assess separation and washing efficiency, hydrophobic interaction, washing fluid compatibility, changes in washing fluid with changes in contaminants. May require preblending for consistent feed. Use the jar test protocol to determine contaminant partitioning.
Metals	Concentration and species of constituents (specific jar test) will determine washing fluid compatibility, mobility of metals post-treatment.
Humic acid	Organic content will affect adsorption characteristics of contaminants on soil. Important in marine/wetland sites.
Other chemical	
pH, buffering capacity	May affect pre-treatment requirements, compatibility with equipment materials of construction, wash fluid compatibility.

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3.1.3 Process Evaluation

The main measure of effectiveness is the ability to meet specified standards so that the treated soil can be returned to the site. The selection of a soil washing system usually then depends on the quality of the oversize materials and coarse grained materials since these will be targeted to be returned to site (Anderson, 1993).

Soil washing performance is closely tied to two essential physical soil characteristics evaluated during site characterisation, *particle size distribution* and *cation exchange capacity*, which should be carefully evaluated in light of the overall site geology and the vertical and horizontal extent of the chemical contamination (Anderson, 1993).

When used as a pre-treatment step for other remediation processes, soil washing presents two important advantages. The first is waste minimisation, which is, concentration of a large proportion of the contaminant into a much smaller residual soil product which will be treated further. The second advantage lies in its cost-effectiveness resulting from the volume reduction of contaminated soil to be treated by other expensive methods (Anderson, 1993).

The fact that the soil washing system can be operated as a closed treatment system, permitting the control of fugitive dusts and volatile emissions, is a valuable asset in securing public acceptance of this new technology (Anderson, 1993).

To really evaluate the effectiveness of this technology, one has to look at specific case studies and the successes achieved there. Some data is shown in Appendix D with reference to amongst other, the range of particle sizes treated, contaminants successfully extracted, by-product wastes generated, extraction agents used, major extraction equipment for each system and general process comments (Boulding, 1996).

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3.1.4 Limitations

The waste matrix may represent the most significant limitation. Complex mixtures of contaminants also make it difficult to produce a single suitable washing fluid and may require sequential washing steps with different additives. Further, frequent changes in the contaminants and their concentrations in the feed soil can disrupt the process, requiring modification of the wash fluid formulation and the operating settings. This can be as a result of inaccurate site characterisation where the material encountered during remediation may not be like the soils studied in treatability and pilot scale tests (Anderson, 1993).

Soil washing will usually not be cost effective in treating soils having a: high percentage of clay and silt (more than 30 to 50%), high humic content or contaminants such as mineralised metals or hydrophobic organics. Efficiencies can be increased by adding chelating agents, surfactants and other chemicals but they may be hazardous and are often difficult and expensive to recover from the washing fluid and the soil causing problems with residuals management. The costs of increased efficiencies and waste treatment should be played off against each other (Anderson, 1993).

The main risk in soil washing operations is that of inaccurate site characterisation, rendering the proposed process inadequate. Site conditions can also pose limitations. For example, sources of process water and electrical power are usually required, permits for wastewater discharge must be obtained, land use approved and sometimes even roadways constructed to remote areas (Anderson, 1993).

3.1.5 Cost Aspect

The major advantage of soil washing from a cost perspective is the ability to reduce the amount of soil to be handled by more expensive methods thereby reducing total remediation costs.

The cost of soil washing is dependent upon several important variables:

- Volume of soil to be treated.

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- Type of contaminants to be removed.
- Particle size distribution (especially volume of fines).
- Site preparation requirements (excavation, infrastructure, utilities).
- Equipment, labour, chemicals.
- Residuals management (re-use, disposal, and maybe valuable extract).

For estimating costs, Table 3.3 can be used as a guideline as it contains the important components (Anderson, 1993).

Table 3.3. Soil washing comparative cost data (Anderson, 1993).

	Volume (Short tons)			
	25 000	**50 000**	**100 000**	**200 000**
Capital Costs				
Plant Capacity	15 ton/hr	25 ton/hr	25 ton/hr	50 ton/hr
Process Time	6 months	9 months	12 months	12 months
Plant Cost ($)	3 000 000	4 500 000	4 500 000	7 500 000
	Prices	**Expressed**	**in $/ton**	
Operating Costs				
Depreciation	40	30	15	12
MOB and DEMOB	8	4	3	1
'Normal' site Prep	12	6	4	2
Material handling	15	15	15	15
Labour	30	25	20	15
Chemicals	15	15	15	15
Maintenance	8	6	4	2
Safety Equipment	3	3	3	3
Utilities	8	8	8	8
Process Testing	15	12	8	5
Disposal of Residuals	32	32	32	32
10% assumption				
Management/Engineering	70	60	48	40
Overhead and Profit				
NET PRICE ($/short ton)	256	216	175	150

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A clear understanding of the site is essential to developing costs for comparison to other technologies. Comparing the costs of this technology with other technologies, projects in the range of 25 000 to 200 000 ton were evaluated. The price range was (in 1993 money) $150 to $250/ton for soil washing, including disposal of sludges, $350/ton for secure landfill and $1 000/ton for incineration, including excavation, site support, gate rate disposal, transportation and applicable taxes (Anderson, 1993).

3.1.6 Future Developments

The focus of future developments will surely be on additional treatment of the fine-grained fractions to reduce the residual material that has to be disposed of off site, reducing the unit treatment prices. Work is underway on bioslurry reactors for use in further degrading the organic constituents in the fines and on developing extraction and recovery techniques to remove inorganics. Improved extraction and recovery may result in recovered contaminants with a market value (Anderson, 1993).

Although soil washing will undoubtedly continue to be offered in mobile configurations, it has been shown in Europe that fixed-based plants are more efficient. The major problem here being the ultimate disposal of residuals generated (Anderson, 1993).

3.1.7 Process Integration

Although individual unit processes may be suitable for treating a wide variety of contaminated soils, there are site-specific limitations, often related to either complex mixtures of contaminants or to the nature of the soil constituents, that may make the successful application of the techniques ineffective or uneconomic. Process integration is an approach where a combination of unit process treatments provides a more effective and economic overall treatment. Not only can this approach extend the range of treatable contamination problems; it can reduce the treatment cost of complex contamination by allowing maximum use of low cost treatments, therefore reserving the higher cost methods for a more limited volume of material (Martin &

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Bardos, 1994). The main objective is thus to enhance soil treatment by extending the potential application of individual methods beyond that where they would normally be used as a single, stand-alone treatment (Wood, 1997).

The individual processes can be used for either pre-treatment or treatment or a combination of the two, depending on the downstream processes. The processes can even run side by side with the attributes of one process being simultaneously exploited by another process. The upstream treatment aims to enable the downstream process to be more efficient and cost effective by:

- reducing the volume of soil,
- improving access to the contaminant,
- changing the form of the contaminant,
- changing the phase of the medium holding the contaminant,
- changing the concentration of the contaminant,
- treating or containing mobile contaminants, and
- simplifying complex contamination (Wood, 1997).

Process integration can encompass a variety of scenarios, for example: combining in-situ systems, combining ex-situ processes, separating contaminated materials into more readily treatable fractions and combining soil treatment with waste treatment.

Bioventing is an example, where two in-situ processes are combined, bioremediation and soil venting. A significant problem for in-situ biological treatments has been to supply the active microbial population with sufficient nutrients and oxygen. Soil venting is a physical technology where air is pumped through the contaminated soil to maximise the volatilisation of organic compounds. Together, the oxygen is delivered far more efficiently to the micro-organisms and biodegradation rates increase. It has been used effectively to clean up petroleum hydrocarbon contaminated sites (Martin & Bardos, 1994).

Another example is the combination of soil washing with chemical extraction to meet required clean up levels. The extraction process can remove residual contamination and be used to remove the contaminants from the fine fractions separated by soil

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washing. Soil washing has also been combined with an ex-situ bioslurry reactor to treat a fraction enriched with polyaromatic hydrocarbons separated by the plant. The reactor was optimised for the treatment of fine clay and silt particles and therefore benefited from the particle sizing achieved by the washing plant (Martin & Bardos, 1994).

This study eventually also aims to be part of an integrated treatment system for hydrocarbon contaminated soils. Soil washing as described here will be used as pre-treatment after which the residual contamination will be removed biologically by means similar to those used by van Zyl (1997). This will result in a faster and more economic treatment for the problem at hand.

3.2 IMPINGING JET REACTORS

The kinetics of a heterogeneous chemical reaction is dependent on the reaction rate and the rate of mass transfer between the phases. Considering reactions where the mass transfer step is rate limiting, an increase here will improve the overall kinetics of the reaction significantly. Improving phase contact is a big part of chemical engineering research in all concerned fields due to the high potential economic gains. Of course the more turbulent the mixing, the higher the mass transfer and this is precisely how the idea of impinging jet reactors evolved. This technology uses the kinetic energy of the feed streams to create turbulent conditions and thus enhance the mass transfer (Botes, 1995).

The essence of the method of impinging streams lies in the flow of two or more streams towards one another and the impingement at the midpoint of their flow, the so-called impingement plane. The inertia associated causes a repeated penetration through the impingement plane into the opposite stream until discharge. This unique configuration causes a significant enhancement of the heat and mass transfer processes. It covers homogeneous systems such as gas-gas and liquid-liquid as well as heterogeneous systems like gas-solid, gas-liquid and solid-liquid for example: drying, dust collecting, mixing, adsorption, dissolution of solids, combustion of gases, liquids and solids, ion exchange and extraction. This technology is thus very versatile and it

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is estimated that almost any process in chemical engineering can be carried out more efficiently and with a lower power input in comparison to conventional methods (Tamir, 1994).

The process of mass transfer is generally governed by certain resistances. The aim then is to reduce these resistances and promote transfer. In this study no reactions will occur, instead the contaminant is physically washed off the soil by the water. In the case where chemicals are added to enhance the soil washing efficiency, the principles of jet reactors associated with chemical reactions will however, be invaluable and should thus not be forgotten. The main principle of interest here is the highly turbulent region (impingement plane and close surroundings) that is formed when the streams collide.

Three processes are responsible here for removal of the contaminant. Firstly, the phase contact between the water and the diesel is increased which helps transfer of the diesel to the washwater even though the solubility of oil is low in water. Secondly, the high-pressure water jet stream is able to 'tear' some of the contaminant off due to the shear forces present. Lastly, in this region the high concentration of particles, combined with the very turbulent mixing (due to the collision of the high velocity streams) that occurs, creates the ideal environment for the scrubbing action required to physically remove the contaminants from the soil surface. The high-pressure water jet system is thus an ideal candidate to improve soil washing efficiencies thus far achieved.

Another advantage is that further liberation might occur and lumps of soil broken up to expose a greater area to the washing process ensuring a more complete washing process. This will also aid in separating the highly contaminated fines from the clean fraction. Silt and clay particles tend to attach to sand and gravel particles by physical processes such as compaction and adhesion and the jet may be able to separate them.

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3.3 SELECTIVE SOFT SELF ATTRITION

The Selective Soft Self Attrition (SSSA) process was developed to reduce the leaching times of gold ores and decrease the grade of undissolved gold in the ore residue (can also be used for Uranium, Copper, Lead or other minerals from an ore which is softer than the surrounding mother ore). Success has been achieved in treating slime dam residues, the tailings from plants and calcines of pyritic concentrates (Sharp, 1993).

The milled ore, in which the gold-bearing minerals are completely liberated (a pre-requisite), is stirred at high speed in a pulp of high density. The gold-bearing minerals are softer than the surrounding quartz, therefore the rubbing action of the interparticle movement, caused by the agitation, has the effect of selectively grinding down the gold-bearing ore, allowing for faster and more complete leaching. The harder ore fractions thus effectively act as grinding agents on the softer gold bearing ore. The aim here is not further liberation of the gold and so the process will have little effect on the particle size distribution in the ore (Van Zyl, 1995). Due to the scrubbing action, any coating of cyanide-impervious deposits is also wiped off leaving a clean particle surface for further treatment. The process operates at much higher pulp densities for much shorter dissolution times producing lower residues with lower power consumption than previously used methods. This means that the gold asymptote residue values can be obtained quicker, easier and cheaper (Sharp, 1993).

The apparatus is very simple and only consists of a cylindrical container in which the attrition stirrer operates. The stirrer is of novel design in that the stirrer blades are not solid, but instead comprise of a series of vertical stainless steel rods (see figure 3.3). This causes a movement of the particles in the pulp relative to one another producing the attrition.

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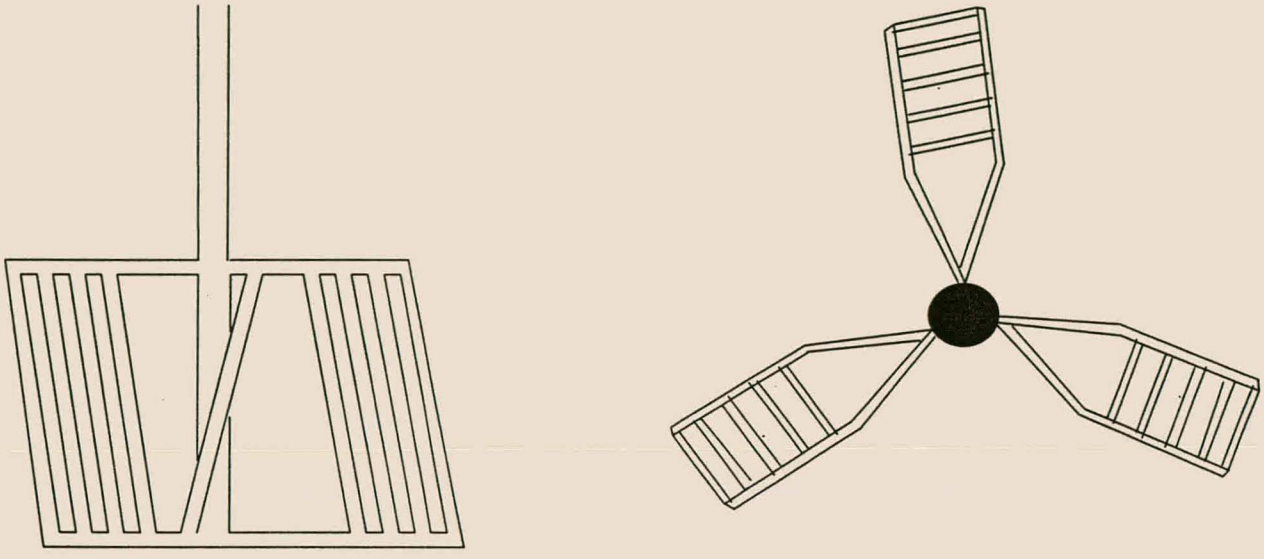

Figure 3.3. Attrition Stirrer Side and Top view

During attrition, the centre of the container is entirely void of pulp (see figure 3.4). The pulp is stirred around, and at the same time is thrown upwards against the container walls by the angle of the attritor arms. From here, it folds back over the attritor arms under gravity, thus causing a continual homogeneous movement of the pulp throughout the container (Van Zyl, 1995). Baffles can also be added to throw back the pulp from the sidewall of the container into the inner parts of the stirrer. This causes the pulp to pass repeatedly through the area of the vertical rods and up the sidewall again, ensuring the relative movement of the particles in the pulp that is required for attrition. A slight increase in temperature during the attrition is a good sign, as it means that the pulp density is high enough and the attrition efficient. The process is very sensitive to pulp density and a small amount of water added can change the consistency completely (Sharp, 1993).

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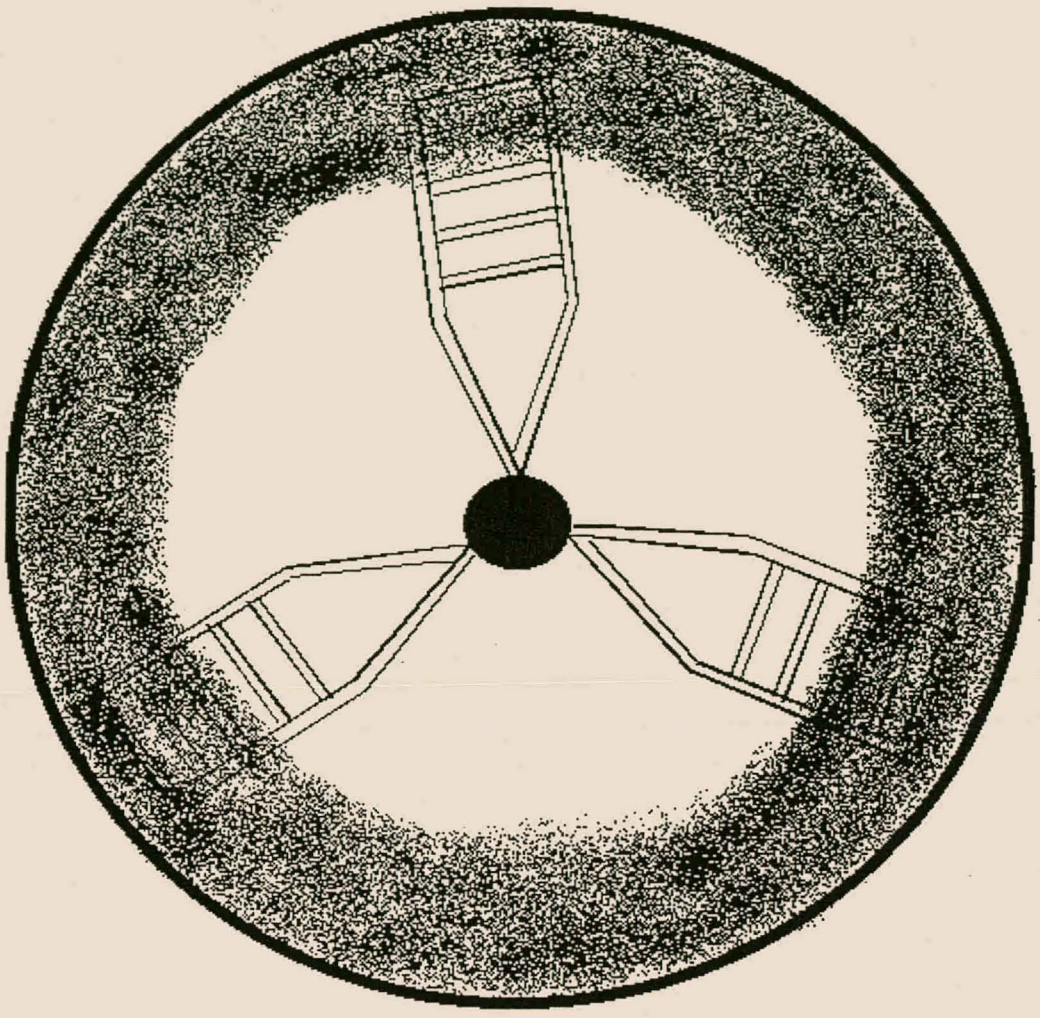

Figure 3.4 Movement of pulp in the container

With reference to the problem at hand, the softer parts (or coatings) will now be the oil contaminant. The interparticle attrition should thus scrub the oil off the sand.

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CHAPTER 4

EXPERIMENTAL

4.1 IMPINGING JET REACTOR

Apparatus

Figure 4.1 represents the apparatus used to perform the jet reactor experiments.

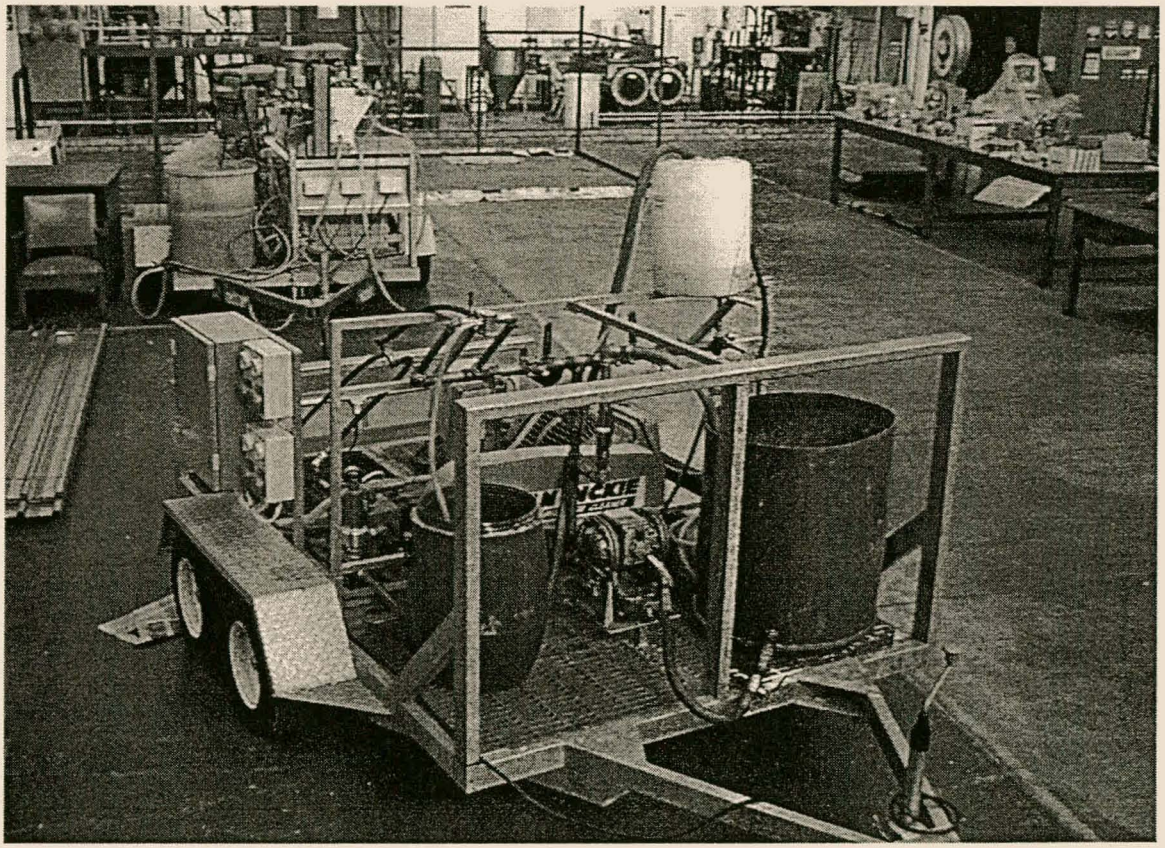

Figure 4.1. Jet Reactor Apparatus

To aid in the following discussion, figure 4.2 shows diagrammatically the jet reactor apparatus.

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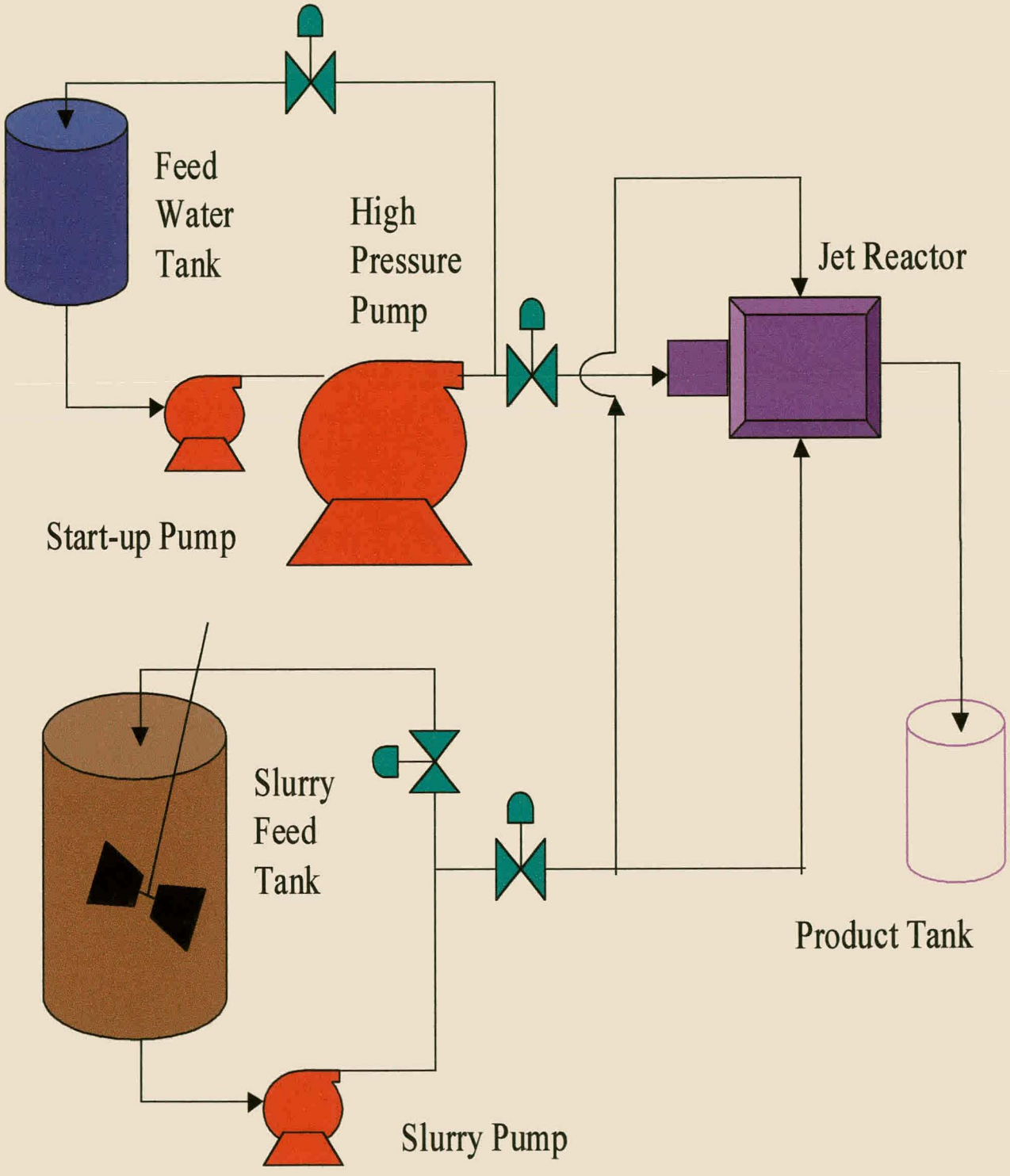

Figure 4.2. Diagram of Jet Reactor Apparatus Set-up

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The reactor itself is constructed of two halves (see figure 4.3), machined out of stainless steel, and bolted together. This enables cleaning the inside of the reactor and replacement of worn nozzles. Nozzles used are constructed of stainless steel with tungsten-carbide spray heads. The spray head opening on the nozzles used are 0,0457 mm (0,018 inch). The high-pressure pump is a positive displacement pump, the slurry pump is a peristaltic pump and the start-up pump a centrifugal pump. All lines handling high pressures are constructed of material suited to handle these pressures. The slurry feed tank stirrer is an industrial stirrer with propeller type blades. All tanks used are cylindrical steel or plastic containers.

In short, the apparatus functions as follows (refer to figure 4.2): The slurry is created in the slurry feed tank from where it is pumped to the reactor by the slurry pump. The high-pressure pump feeds water from the water feed tank to the reactor through the nozzle. The washing takes place inside the reactor and the product is removed to the product tank.

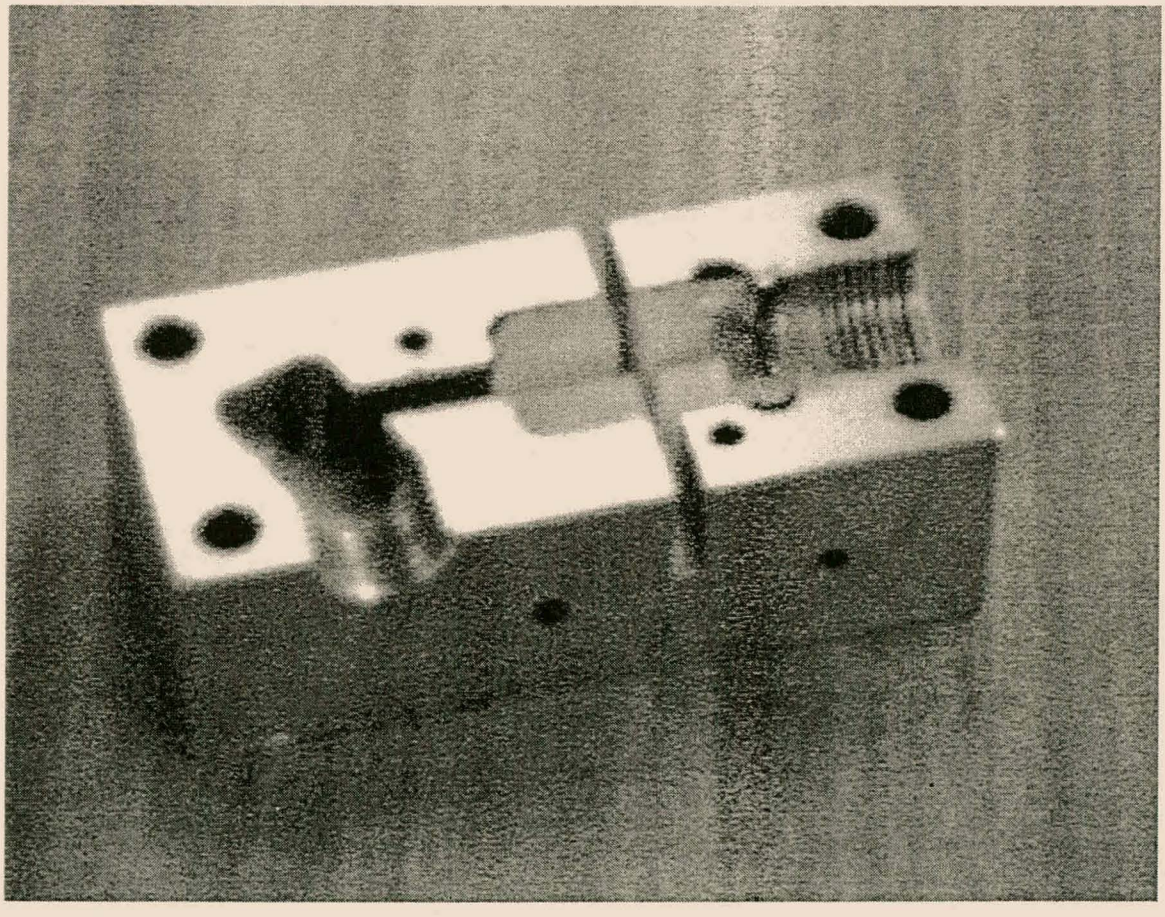

Figure 4.3. Jet Reactor (inside)

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Due to high pressures involved, the first and most important thing to do is to make sure the apparatus is safe. The reactor should be checked to ensure that all the bolts keeping the two halves together are tight and that the high-pressure inlet line is secure to ensure that the reactor does not fail under the high pressures. When any leakage is noticed at this part of the apparatus during operation, it means that the reactor is not sealing properly and attention should be given immediately to the repair thereof.

The high-pressure pump, start-up pump and the slurry pump should be checked. The rest of the apparatus should be checked for leaks that could affect safe operation. Lastly, and very important all the electrical connections should be checked. There are various pieces of electrical equipment being used together with water and any oversight can lead to serious injuries. If the apparatus has been deemed safe, the preparations for the experiments can begin.

Procedure

Starting with the slurry, the contaminated sand is mixed with water in the feedtank to the desired solids concentration. A stirrer is used to mix the slurry and suspend the sand particles so that it can be pumped. Next, the water feedtank is filled.

The electrical part of the apparatus has been modified such that a single three-phase cable supplies electricity to the unit. The only part of the unit not using electricity is the peristaltic pump that has to be connected to compressed air. Once everything is connected, the experiment can begin.

The stirrer is switched on and within a few seconds the slurry is ready to be pumped. The apparatus is designed so that both the slurry and the water are pumped in recycle loops before being fed to the reactor by use of the appropriate valves. Opening the valve from the slurry feed tank to the slurry pump (with the valve from the slurry pump back to the feedtank open), the slurry is recycled and now ready to be fed to the reactor.

The high-pressure pump needs a little start-up pump and this centrifugal pump is situated between the water feed tank and the high-pressure pump. The valve from the water feedtank to the pumps are opened and the pumps then switched on sequentially

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so that the water is recycled (the valve from the high-pressure pump back to the feedtank open) and is ready to be fed to the reactor.

By only feeding the water from the jet feedtank to the reactor at the desired pressure, the jet flowrate corresponding to that pressure can be determined by measuring the flowrate out.

As a result of the reactor configuration and the delicacy of the nozzle, the water has to be fed to the reactor first to ensure that none of the sand particles from the slurry blocks the nozzle. After the water has been re-routed to the reactor (by opening and closing the appropriate valves), the same can be done with the slurry. They now violently collide inside the reactor for as long as deemed necessary while the outflow is removed to the product tank.

To stop the experiment all the above has to be done precisely in reversal. First, the jet stream as well as the slurry are re-routed to recycle. The valve to the slurry pump is closed, the compressed air disconnected and the stirrer switched off. The water pumps are switched off, first the high-pressure pump, then the start-up pump and lastly the valve from the water feedtank is closed.

After each run, the product in the product tank was weighed. Decanting the liquid, the remaining sand was also weighed. This was used in later calculations, together with the jet flowrate measured previously, to determine the actual solids concentration in the reactor (see Appendix A1, B). The product (sand) can now be analysed.

If no further runs are intended, the unit should be flushed with water and everything disconnected.

4.2 SELECTIVE SOFT SELF ATTRITION

Apparatus

An industrial drilling machine with variable speed settings was used to power the stirrer and the special attrition stirrer operated in a cylindrical steel container.

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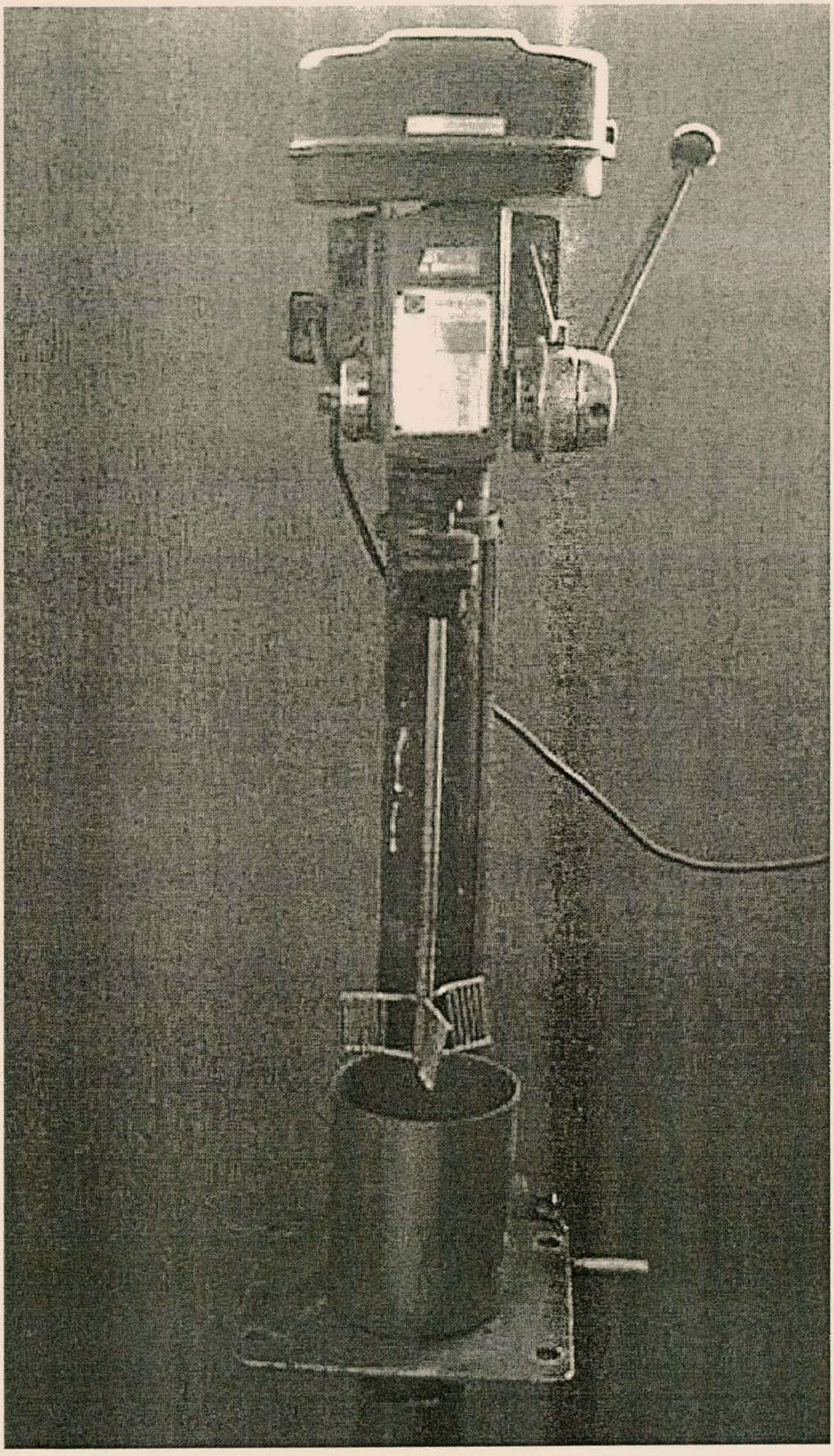

Figure 4.4. SSSA Apparatus

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Procedure

The contaminated sand is mixed with water in a cylindrical steel container creating the slurry. Solids concentration being very important, the sand is weighed and the water measured beforehand. The stirrer is submerged in the slurry and switched on. The stirrer speed being set before the specific experiment to the desired setting. After the required attrition time, the stirrer is switched off and the sand removed for analysis

4.3 TEMPERATURE INFLUENCE

To determine the influence of temperature on the system, the following set-up was constructed.

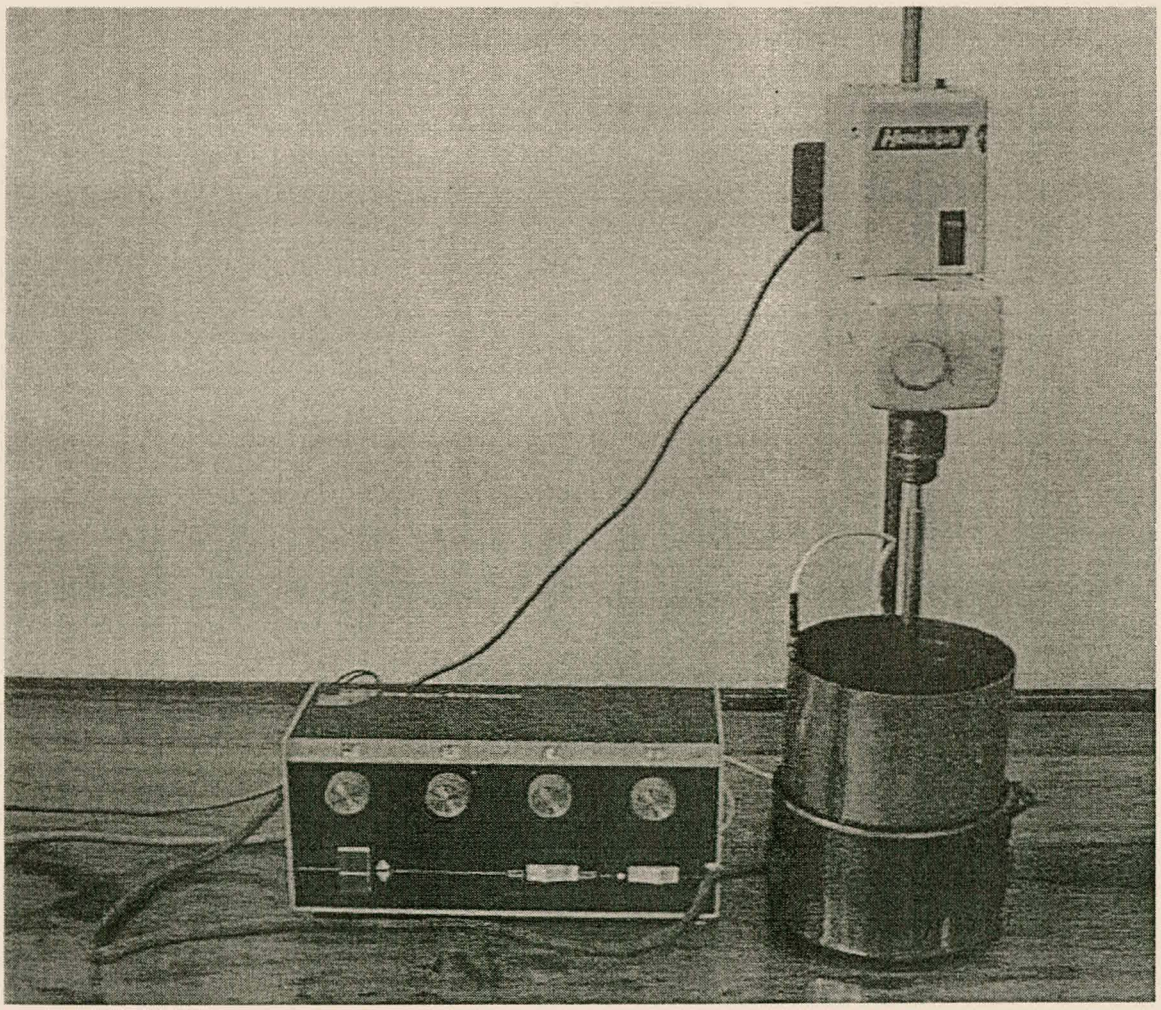

Figure 4.5. Overhead Stirrer, Heating Mantle and Temperature Controller

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The same cylindrical container used for the attrition experiments was used here. Measured amounts of contaminated sand and water was placed in the container to create a slurry. An overhead bench stirrer was used to suspend the slurry. The slurry was kept low (10% solids), so that no attrition would occur. The heat was supplied by an electrical heating mantle that fitted around the container. This heating mantle was connected to a temperature controller which regulated the temperature of the slurry by using the signal from a thermocouple immersed in the slurry to regulate the energy input. The temperature of the slurry should be kept constant. After the run was completed, the washwater was decanted and the sand analysed.

4.4 ANALYTICAL PROCEDURE

To ensure accurate and repeatable results a stable analytical protocol had to be established. Numerous methods were encountered in the literature but none were described or found to be very repeatable or accurate in their entirety (Flowers et. al.,1984; McGill & Rowell, 1980).

The greatest problem arose with the volatility of the diesel, both in the spiking of the sand before the experiments and the analysis afterwards. Variations in results of up to 40% were found when this was not taken into account. Therefore, standard methods, slightly altered to reduce the volatilisation problem were used so that results were indeed repeatable. The methods are described below:

4.4.1 Soil Preparation

Due to the volatile components in diesel, a significant amount can evaporate. Therefore, the diesel used was left open to the atmosphere for at least 2 days before it was mixed with the sand. This allowed all the evaporation, which would significantly influence the results, to take place. The soil was then contaminated with diesel on a mass percentage basis and again left for a couple of days prior to use. This procedure aided in stabilising the results, by only including those components that are

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permanently adsorbed and prevented an overestimation of the process efficiencies due to species evaporated and not washed off.

In the first experiments, it was found that if the sand was contaminated with more than 5% diesel, some free diesel remained. Free diesel refers to the diesel not adsorbed onto the sand and remaining as liquid puddles after mixing. As this study is concerned with the removal of adsorbed contaminants, a too high contamination level will produce false results because the free diesel will be floated off and not washed off. The saturation of the sand depends on the particle size distribution. Table 2.3 summarises the four types of sand used (Refer to Appendix C for size distributions). To compare results, it was decided to use a contamination level of 5% throughout.

Table 2.3. Types of sand used in this study.

	Industry Name	Average Particle Size	New Name (to be use in this thesis)
1.	No. 1 Foundry sand	0.51 mm	500 μm
2.	AFS 35 Foundry sand	0.35 mm	300 μm
3.	No. 2 Foundry sand	0.12 mm	100 μm
4.	Silica 300 mesh	0.01 mm	10 μm

4.4.2 Sample Preparation

After the experiment was completed, the washwater (containing the diesel that had been washed off) has to be separated from the sand. This was performed by simply decanting the water. About 250 grams of the sand is then transferred to a small container (in the case of the jet experiments where large amounts of sand were present, two samples were sometimes taken to confirm results, apart from the normal procedure of duplication of experiments). Water is added and decanted a couple of times to free and float all the trapped diesel. The sand is then vacuum-filtered with clean water to ensure that all the free diesel is removed as well as reducing the moisture content that can possibly influence results.

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4.4.3 Soxhlet Extraction

It is important to determine the temperature and extraction time needed for successful and complete extraction. A time of two hours was initially taken from literature and it proved sufficient. When the temperature was too high, an excess amount of the solvent was vaporised. The condensers could not handle these high quantities and it was thus lost to the atmosphere. By keeping the heating elements close to the boiling point and checking to see whether any solvent is lost (measuring before and after without extraction) the optimum settings on the heating mantels were determined.

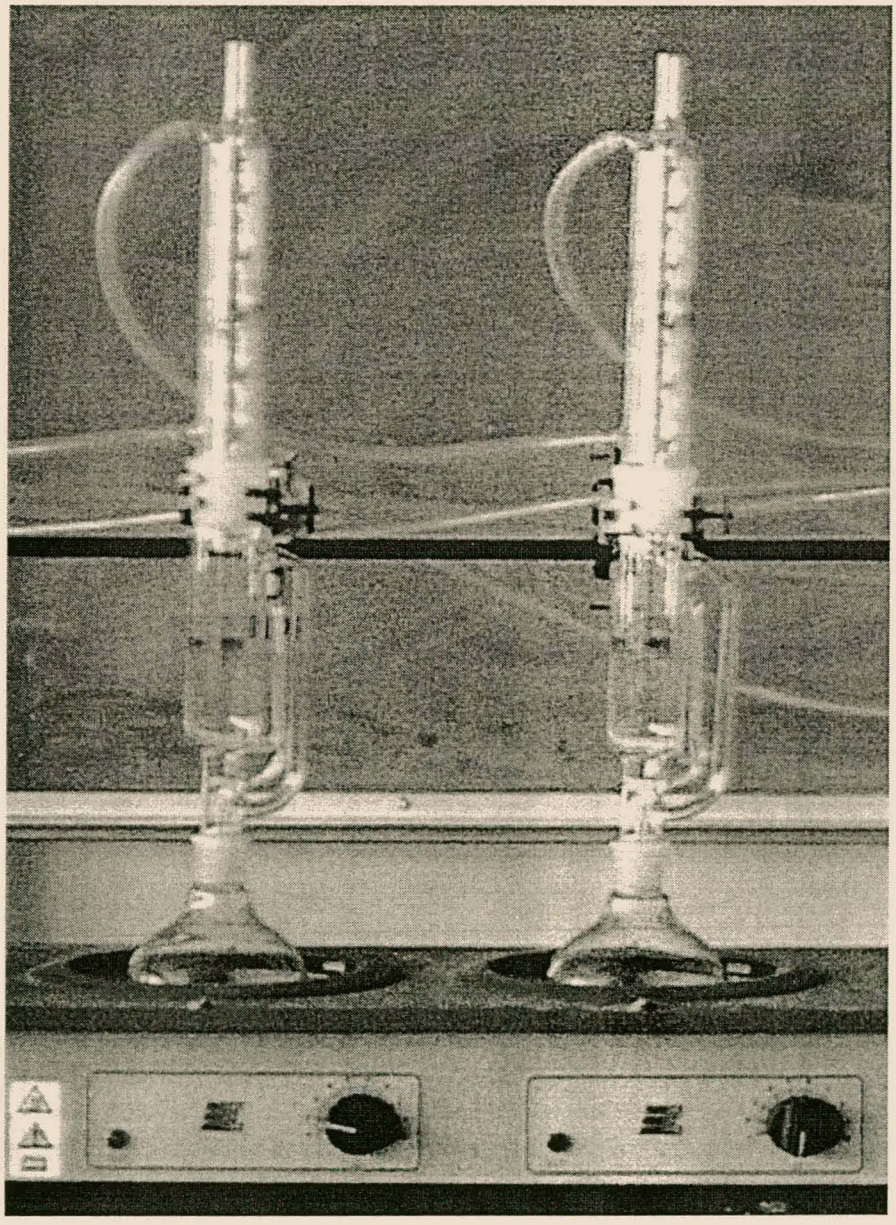

Figure 4.6. Soxhlet Extraction Apparatus

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Fifty Grams (50 g) of the filtered sand is weighed off in a cellulose extraction thimble. Fifty Grams (50g) was used because the larger the sample, the more representative the sample (the thimble could also not handle larger quantities). The thimble is then placed in the Soxhlet unit and the diesel extracted using about 200 ml of Methylene Chloride (MCl) for two hours. Numerous other solvents were considered and these results as well as the literature proved MCl to be the most suitable. This extract is then transferred to a 200 ml volumetric flask, which is filled to the mark with clean MCl.

4.4.4 MCl Evaporation

Lastly, 25ml of the diesel-MCl mixture is allowed to evaporate from a covered petri dish in a fume hood. Because of the high solubility of diesel in MCl and the low boiling point of MCl it is very important to cover the petri dish with a lid to slow down the evaporation, otherwise noticeable amounts of the diesel are lost in this stage (see Appendix A4). After evaporation, the diesel residue is then weighed and the amount of diesel present on the sand is determined gravimetrically (see Appendix A4).

4.4.5 GC-Analyses

Both the 'pure' diesel (diesel used to contaminate the sand) and the diesel extracted (in the Soxhlet apparatus) from the sand after the cleaning processes, were analysed with a Hewlett Packard G1800A gas chromatograph. The column used was a BPI PONA (50m*0.15mm*0.5um) column and the carrier gas was Helium at a flowrate of 0.3 ml/min. The solvent used was MCl and the program looked as follows:

Inlet:	280 °C
Detector:	300 °C
Splitinjection	
Temperature:	100 °C, 3 minutes
	10 °C/min increase in temperature
	250 °C, 10 minutes

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The output was a chromatogram on which the major species could be identified from the peaks obtained. Identification was done by Mrs. H. Botha. The area under each peak is an indication of the concentration of that species in the solution. Together with the chromatogram, these areas as well as area percentage contributions of each selected species were obtained, and used in further calculations (see Appendix A5).

4.4.6 Data Analyses

All experiments were performed at least twice to ensure repeatability. The average of the values obtained was used to quantify the influence of the variable and are shown as the data points on the graphs in the next results chapter. The statistical error band around the data points is of such a nature that trends identified are statistically valid except where specifically stated (see Chapter 6), as some variables had a very small effect over the range tested but insight into the process identified likely trends important for future research.

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CHAPTER 5

RESULTS AND DISCUSSION

5.1 ANALYTICAL PROCEDURE

The following experiments were performed to quantify and evaluate the analytical procedures followed in the testwork, i.e.:

- Pure Diesel Evaporation
- Diesel on Sand Evaporation
- Evaporation of MCl
- Soxhlet Extraction and Evaporation

5.1.1 Pure Diesel Evaporation

Diesel is composed of a large number of species and has a significant volatile fraction. This property can influence results greatly if not kept in mind and compensated for.

An amount of the diesel to be used in the experiments was placed in an open beaker and weighed at intervals (see Appendix A4). As can be seen from figure 5.1, basically all the evaporation takes place in the first day. It is also important to note that more than 40% (by mass) of the diesel is lost due to this evaporation. This will play a significant roll in real spills and should be taken into account.

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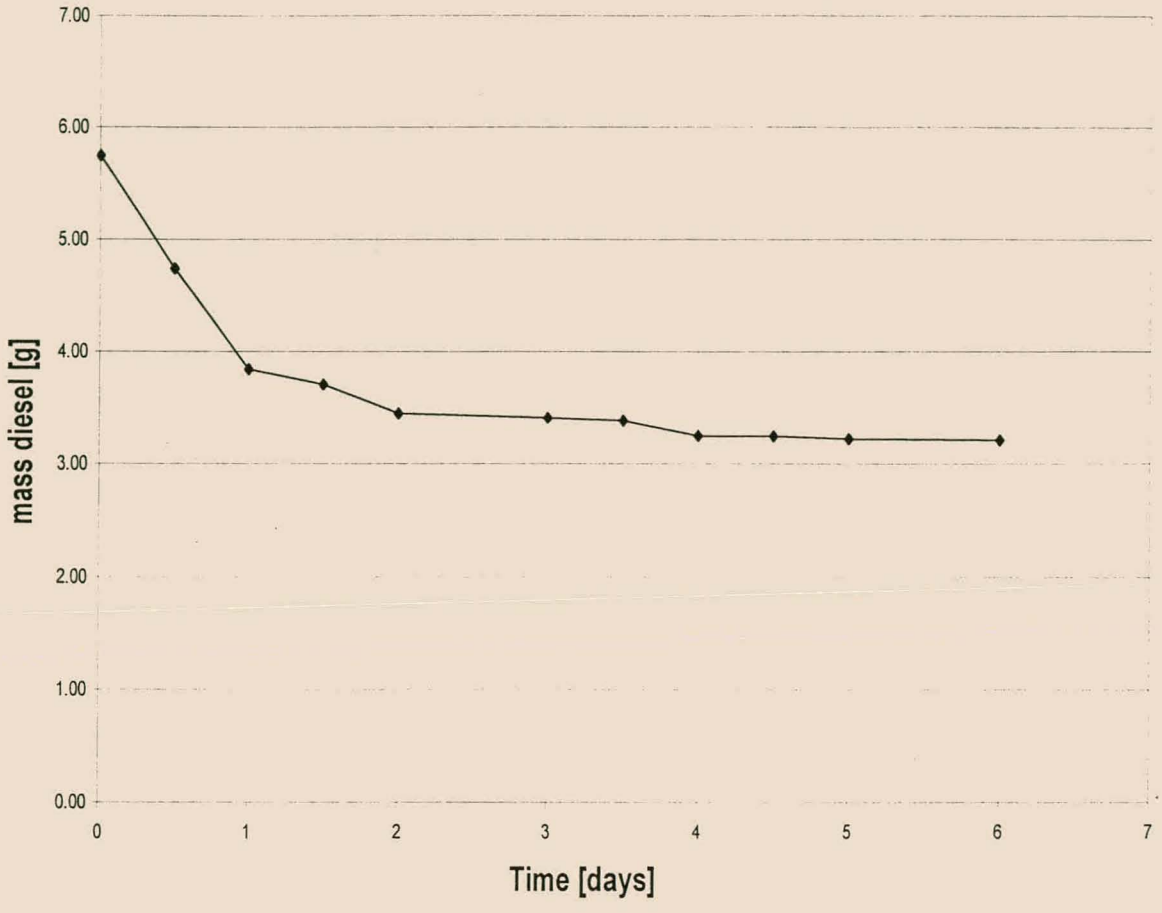

Figure 5.1. Pure Diesel Evaporation

5.1.2 Diesel on Sand Evaporation

When the diesel is mixed with the sand, the evaporation of the diesel is altered. Comparing figure 5.2 with figure 5.1 it can be seen that the evaporation now takes much longer (8+ days) but that again a large amount (48%, by mass) is lost. The evaporation takes longer because the diesel adsorbs onto the sand particles and not all particles are in contact with the atmosphere. The volatile components were able to reach the gas-solid interface easily for the case of pure diesel in a beaker (liquid), but this migration is much more difficult (thus slower) for adsorbed diesel in a sand heap (especially bottom particles). If the contaminated sand were mixed regularly, the evaporation would have been faster, as all the sand particles would have come in direct contact with the air. This sand was however, kept in a container (simulates real

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conditions better). The evaporation rate will however, never approach that of pure diesel due to the adsorptive forces.

These evaporation rates vary with type of soil and particle size. The type of soil and particle size determines the type of bond formed with the diesel. Fine soils (clays) and soils with a high humic content, will form stronger bonds than sandy soils.

Similar experiments should be done to establish site conditions at a spill. The importance in the context of this study is to ensure that the process's efficiencies are not over estimated by including volatiles, and to stabilise later analyses by minimising the evaporation influence as much as possible through the above mentioned pre-treatment procedure.

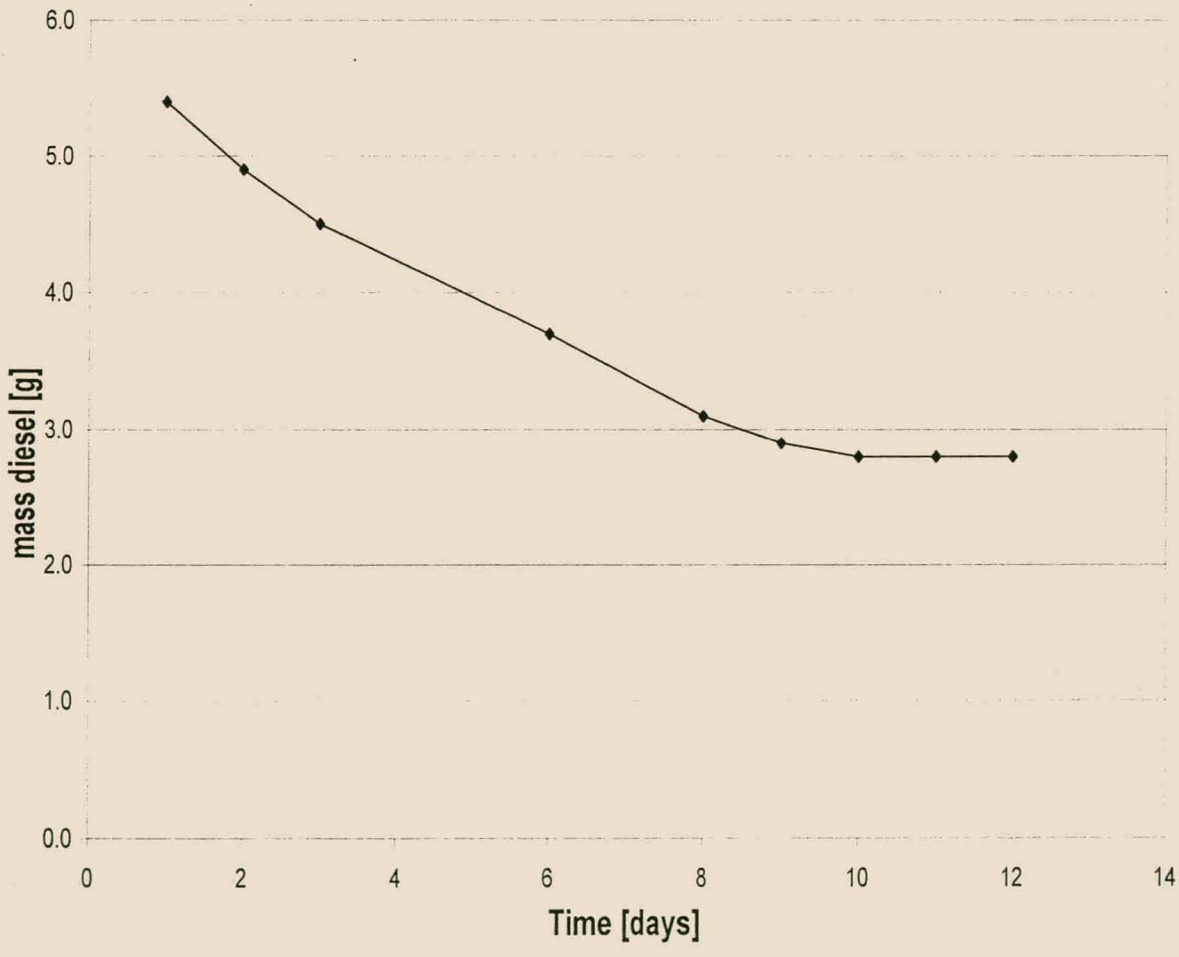

Figure 5.2. Diesel on Sand Evaporation

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5.1.3 Evaporation of MCl

Two standards were made up by mixing known amounts of diesel with MCl in a 100 ml volumetric flask.
Standard 1: 1.7555g
Standard 2: 4.4856g

25 ml of the solution was left to evaporate from a petri dish in a fumehood.

Looking at the evaporation itself, it could be done either with/without a lid (lid does not seal tight, just fits over petri dish) and the extractor fan in the fumehood could be switched on or not.

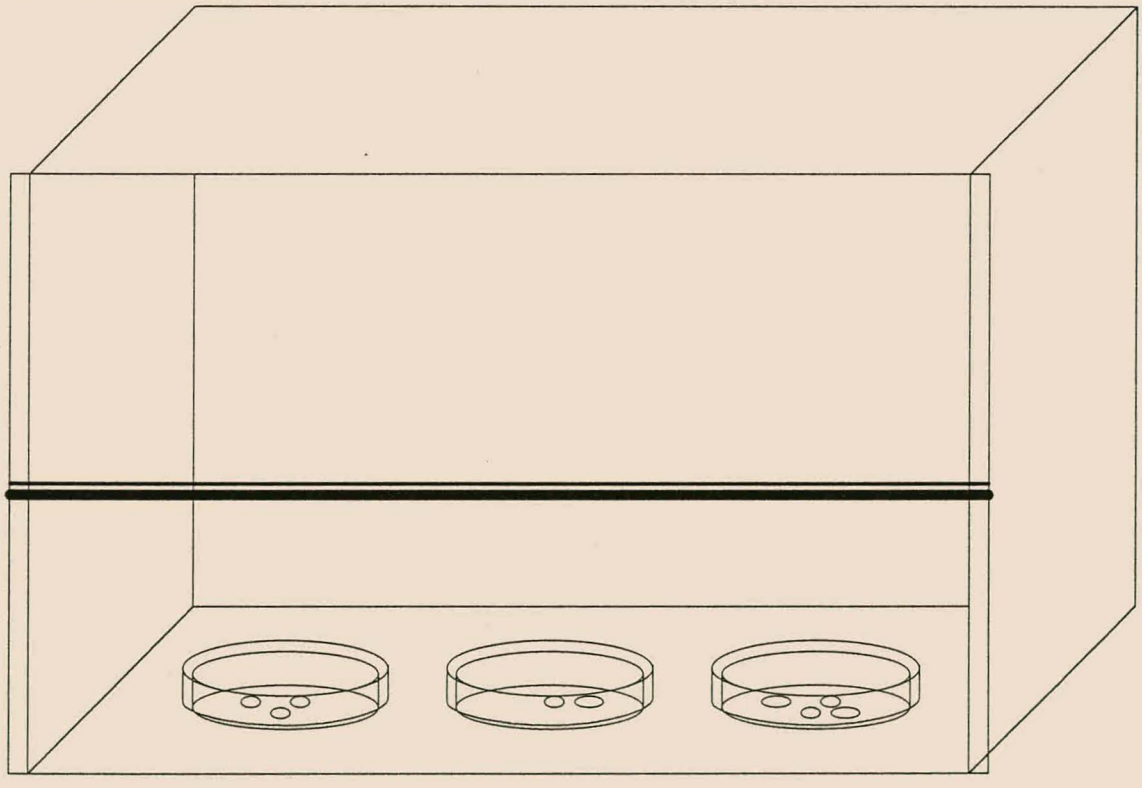

Figure 5.3. Experimental set-up used for the Evaporation of MCl

The residue was weighed and checked against that expected if no diesel had evaporated. This was done to determine the validity of such a procedure. The amount of diesel left from with reference to that expected (from the standards mentioned above) are shown in tables 5.1 and 5.2 as percentage values.

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Table 5.1. MCl Evaporation test for Standard 1

Standard 1

Percentage of diesel left after evaporation (100% = no diesel losses)

	with fan	without fan
with lid	84%	97%
without lid	53%	

Table 5.2. MCl Evaporation test for Standard 2

Standard 2

Percentage of diesel left after evaporation (100% = no diesel losses)

	with fan	without fan
with lid	92%	98%
without lid		75%

First, and somewhat surprisingly, it can be seen from the tables (keeping the huge difference in boiling points of the diesel and MCl in mind), that large amounts of the diesel are lost if the evaporation is not controlled. The more the evaporation is suppressed, the less diesel is lost. It was therefore decided to do the evaporation with a lid and without the fan to keep results as accurate and repeatable as possible. These losses of diesel can be explained if one remembers that MCl was chosen specifically because it is such a good solvent, and that the boiling point of MCl is very low (39 °C, making it extremely volatile). The combination of these factors will result in large amounts of the diesel lost if the evaporation is not controlled.

5.1.4 Soxhlet Extraction and Evaporation

To ensure that the analytical protocol gave the most accurate and repeatable results, the whole process had to be examined over the range of expected values. The evaporation part had been examined previously, and here it was combined with the other important part, Soxhlet extraction. Three standards were made up by mixing known quantities of sand and diesel:

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- Standard 1: 0,1 % (1000 ppm)
- Standard 2: 0,5 % (5000 ppm)
- Standard 3: 1,0 % (10 000 ppm)

These were then subjected to Soxhlet extraction and subsequent evaporation and compared to the values expected. Results are shown in table 5.3.

Table 5.3. Total Analytical Procedure tests

	Std 1	Std 2	Std 3
Percentage diesel left	89	91	86

As can be seen from the table, more of the diesel is indeed being lost in the other crucial part (Soxhlet extraction) of the analytical procedure. These losses can be attributed to three factors: sampling, not complete extraction and evaporation, of which evaporation would be the most significant. Losses in the complete analyses can be as much as 15%, but this is the most accurate and repeatable method that could be found and was thus, adopted for all experiments. Although results may be underestimated by as much as 15%, this protocol however, delivers repeatable results, something no other method encountered (e.g. GC – analysis, Spectophotometry, etc) could guarantee.

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5.2 IMPINGING JET REACTOR

The following experiments were performed to quantify and evaluate the impinging jet reactor process, i.e. the effect of:

- jet pressure,
- slurry flowrate,
- size fraction, and
- solids concentration.

5.2.1 Efficiency

To measure the efficiency of the process, the amount of diesel (ppm) left on the sand after the washing process, was determined. This was chosen as a measure of efficiency rather than for instance percentage removed because the ultimate goal in remediation is to reach a certain acceptable level of contamination set by legislation. All graphs will use this concept to measure the effect each variable has on the decrease of diesel concentration (efficiency of the process). It will nevertheless be insightful to keep the initial contamination level of 5% by mass diesel (which corresponds to 50 000 ppm) in mind.

5.2.2 Feedmaterial

As mentioned in section 4.4.1, the sand was contaminated with diesel to a level of 5% by mass (which corresponds to 50 000 ppm). This sand was mixed with water in the feedtank to create a slurry. This slurry was then stirred, and pumped in recycle until it was re-routed to the jet reactor, when a run was performed.

This continuous stirring and pumping resulted in most of the diesel being removed in this part of the unit, lowering the actual feed to the reactor to around 2500 ppm (see figure 5.4).

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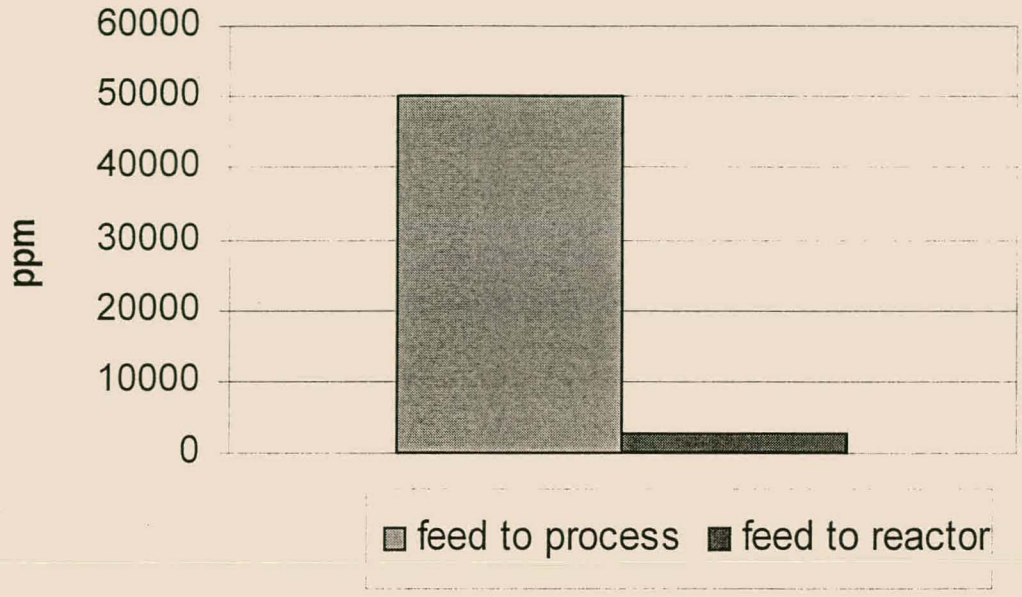

Figure 5.4. Feedmaterial to the process and the reactor

5.2.3 Jet Pressure

In figure 5.5, the effectiveness (in decreasing the diesel contamination) of increasing the pressure (and thus flowrate) of the jet water stream from 10 MPa to 30 MPa is shown in comparison to the sand in the feedtank that has not been through the jet reactor.

Looking at the influence of the pressure, it is surprising that such a big increase in pressure only results in marginally better results. A possible reason for this may be that the reactor configuration is such that the energy of the jet is not being utilised efficiently. The contaminated sand particles is being dragged along with the jet (sort of a venturi effect) instead of colliding with the jet to such an extent that the diesel can be removed by the shear forces created. The turbulence created in the reactor is thus, mostly responsible for the removal.

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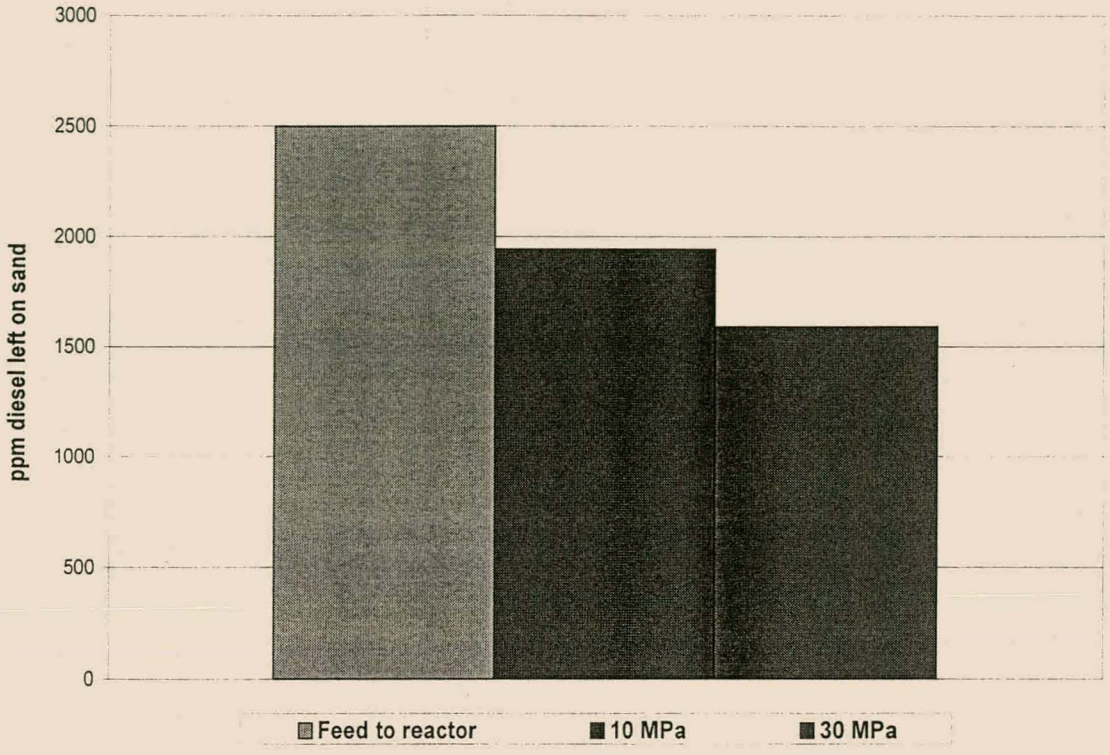

Figure 5.5. Influence of Jet Stream Pressure

Secondly, it is interesting that the sand in the feedtank is almost as clean as the sand that underwent this highly turbulent jet washing. This may appear strange at first, but considering what happens in that part of the process it is quite understandable. Firstly, the slurry is stirred. This imparts energy and thus, removes some diesel. Secondly, the slurry is recycled continuously before being fed to the reactor (by closing the recycle valve and opening the feed valve). This continuous stirring and pumping appears to be efficient enough to remove a significant amount of diesel on its own.

5.2.4 Slurry Flowrate

The influence of the slurry flowrate to the reactor (in decreasing the diesel contamination) is shown in figure 5.6, again in relation to the sand in the feedtank. The highest (26 kg/min) and lowest (16 kg/min) flowrate possible with the slurry pump is shown here and looking at the small difference it was deemed unnecessary to do further experiments.

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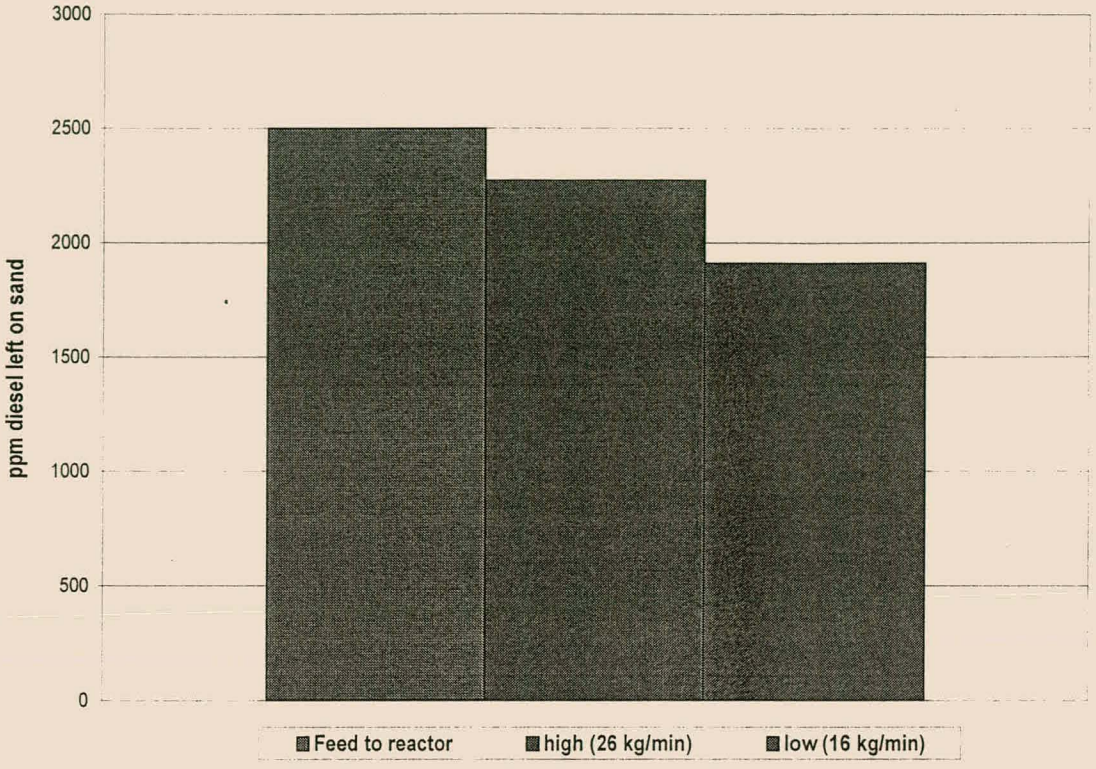

Figure 5.6. Influence of Slurry Flowrate

As discussed above, a large amount of contaminant is removed by the stirring and pumping of the feed.

An increase in removal can clearly be seen as the slurry flowrate decreases. This is due to the contact time of the sand particles with the jet stream. The lower flowrate allows longer and more complete contact of the slurry with the jet stream, although as said previously, this contact could possibly be improved by better reactor design

5.2.5 Size Fraction

The effectiveness of the process on five samples of sand used is shown in figure 5.7. The four types previously mentioned (see Appendix C) were used as well as a mixture of 75% 10 μm sand and 25% 500 μm sand, to represent a 'real' soil that corresponds to a sandy loam soil.

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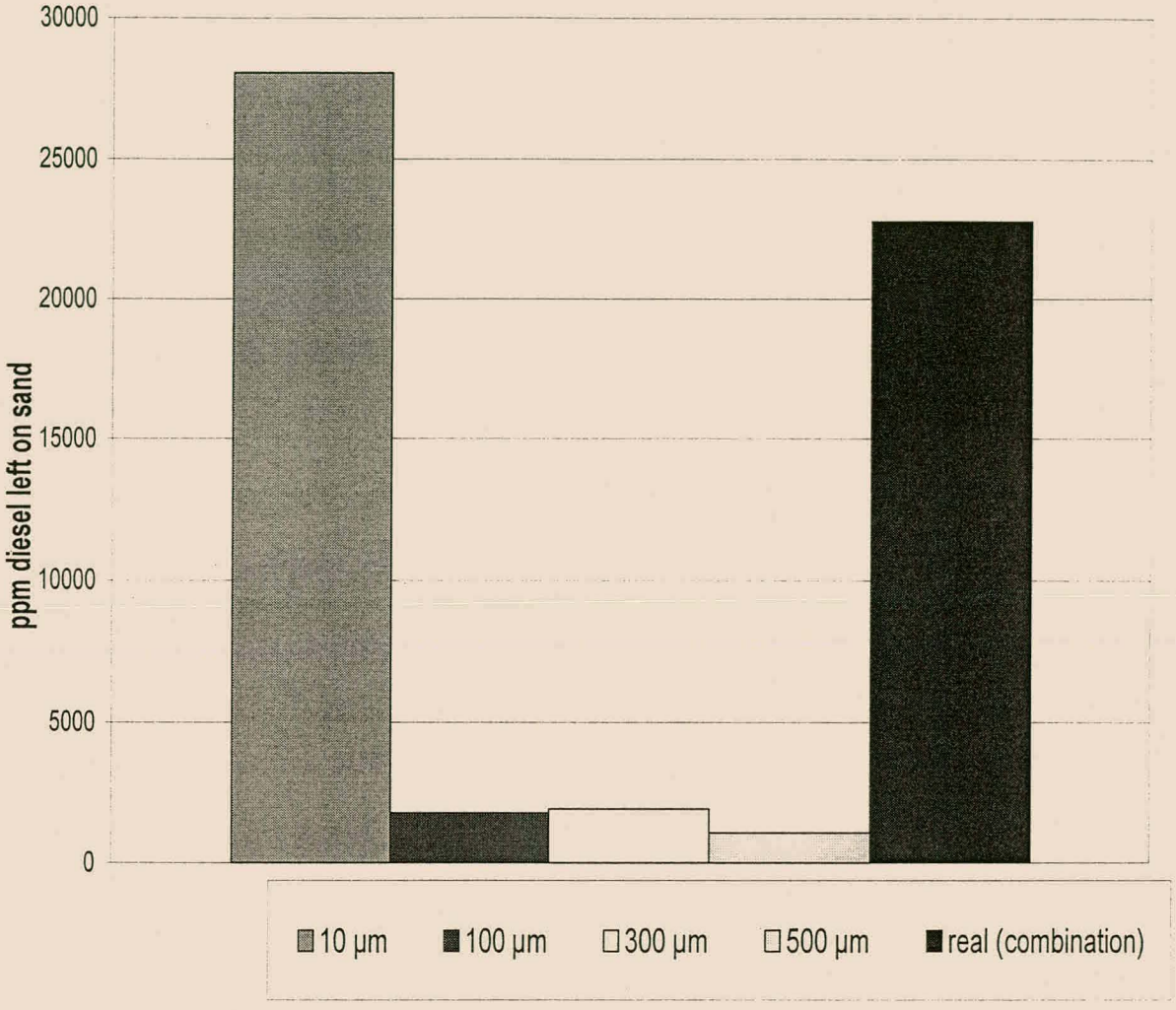

Figure 5.7. Influence of Particle Size

Figure 5.7 shows clearly that for the present reactor configuration there is a lower limit to the particle sizes treatable. The three courser sands (100 µm, 300 µm and 500 µm) are cleaned effectively, but the 10 µm sand (silt sized) and the 'real' soil is merely fed through the reactor without the high-pressure water jet stream having a significant effect. Some diesel is being removed in the feedtank by the stirring and pumping but when it reaches the reactor, it is merely being swept along without effective contact being made between the jet and the sand particles. The larger particles present in the 'real' soil may have a small positive effect by enhancing interparticle scrubbing.

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As expected the larger the particles the more effective the cleaning. Also mentioned previously there is an experimental error in the analyses. These inaccuracies are larger than the difference between the values on this graph. Therefore, the 100 μm sand is in fact not being cleaned more efficiently than the 300 μm sand. The process is actually just that robust that the size difference is hardly recognised and both types of sand cleaned equally well. This is confirmed by results obtained from the attrition experiments (see section 5.3.4).

The importance of size particle fraction on the success of a remediation process is shown clearly here and should therefore always be the starting point when choosing a remediation option.

5.2.6 Solids Concentration

The influence of the solids concentration on the removal of diesel (process efficiency) is presented in figure 5.8 for three types of sand used.

For the largest particles (500 μm), the solids concentration does not seem to have a significant effect. The larger particles being cleaned fairly easy, the influence of solids concentration in the reactor is rather suppressed here (therefore almost a straight line). The upper limit of the solids concentration (15%) was established here by the ability to suspend the particles, so that the slurry could be pumped effectively to the reactor.

For the other two, an interesting effect of this apparatus is observed. Two opposing cleaning mechanisms are at work inside the reactor. Firstly, the jet removes the contaminant by the shear forces of the high pressure water stream but the higher the solids concentration gets, the less effective the contact between the jet and the particles. Secondly, the higher the solids concentration, the more interparticle scrubbing occurs that also removes the contaminant. This is shown effectively in figure 5.8. From 10% to 15%, the efficiency decreases due to the lower contact of the jet with the sand particles, however, from 15% to 20%, the interparticle scrubbing

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becomes dominant, and the efficiency increases again. No curve fitting was done and lines are only included to show the trends more clearly.

It is thus clear that to fully exploit the influence of the jet, the concentration of the slurry solids must be fairly low (10% or less). This is not to say that the interparticle scrubbing process should be neglected. Rather the two should be used in such a way

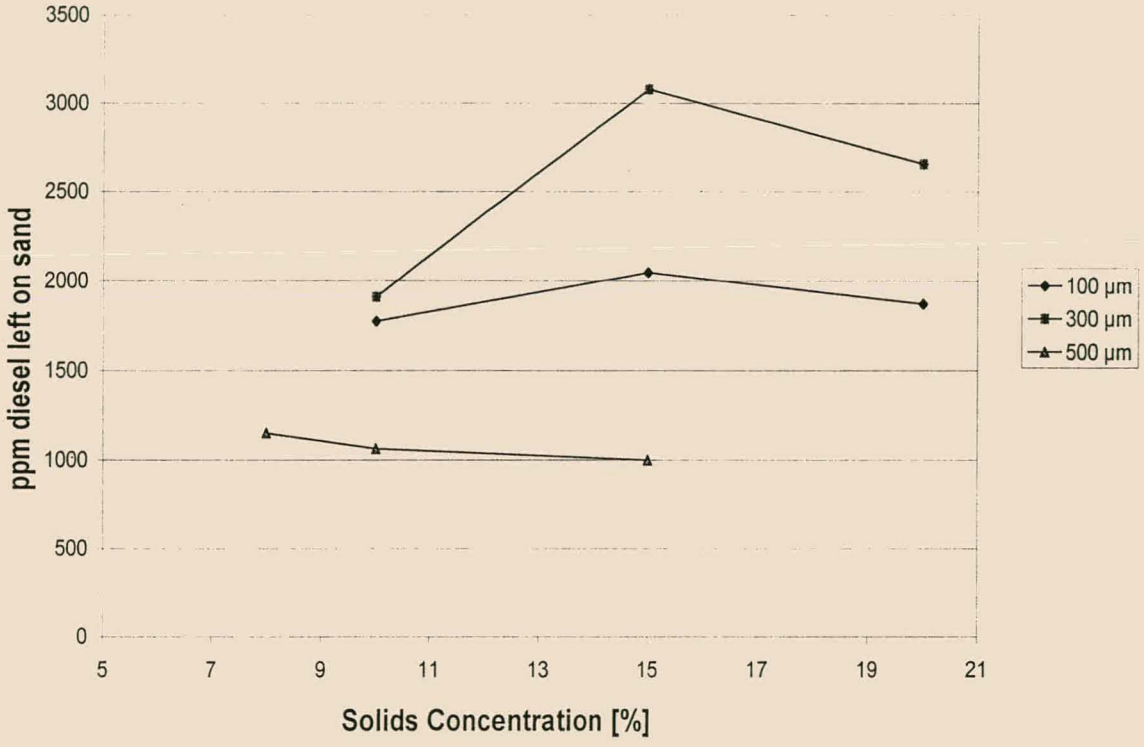

Figure 5.8. Influence of Solids Concentration

that they complement each other, instead of working against one another. This should be kept in mind and used in future designs of more effective reactors.

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5.3 SELECTIVE SOFT SELF ATTRITION

The following experiments were done to quantify and evaluate the selective soft self attrition process, i.e. the effect of:

- solids concentration,
- attrition time,
- size fraction,
- stirrer speed,
- number of stages,
- temperature, and
- combining 2 stages with temperature.

5.3.1 Efficiency

To measure the efficiency of the process, the amount of diesel (ppm) left on the sand after the washing was determined. This was chosen as a measure of efficiency rather than for instance percentage removed because the ultimate goal in remediation is to reach a certain acceptable level of contamination set by legislation. All graphs will use this concept to measure the effect each variable has on the decrease of diesel concentration (efficiency of the process). It will nevertheless be insightful to keep the initial contamination level of 5% by mass diesel (which corresponds to 50 000 ppm) in mind.

5.3.2 Solids Concentration

The whole process of selective soft self attrition relies on the scrubbing of the particles against each other. Therefore, the solids concentration is of utmost importance. Looking at figure 5.9, this importance is clearly illustrated. There is a sharp decrease in diesel concentration (increase in efficiency) from 70% to 80% due to the more effective scrubbing (i.e. more particles). However, a definite optimum exists and this can clearly be seen by the increase in diesel concentration (decrease in

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efficiency) from 80% to 85%. When the slurry becomes too dense, the scrubbing action becomes impeded and the pulp actually moves around as a unit losing the all-important interparticle motion.

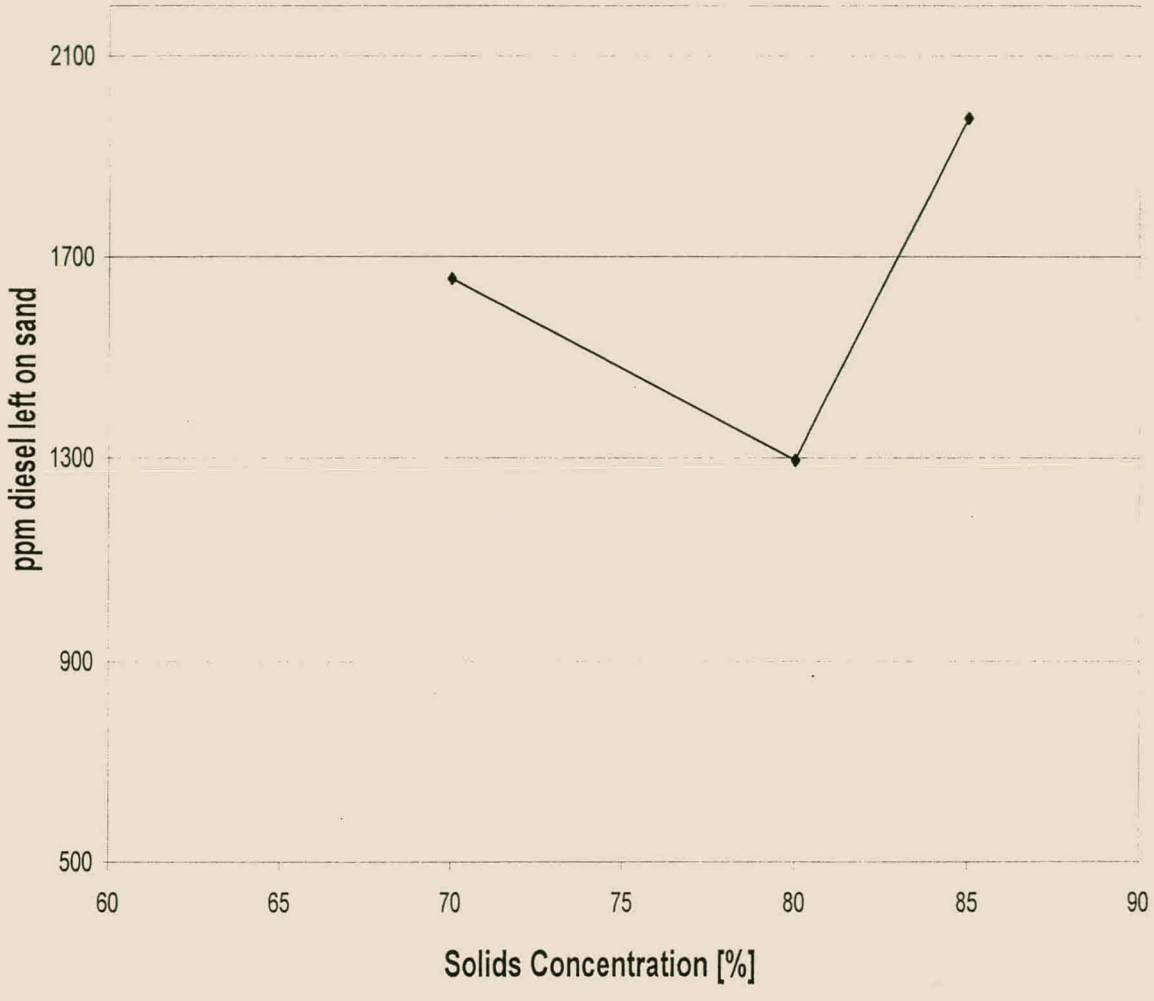

Figure 5.9. Influence of Solids Concentration

No curve fitting was performed on the data, the line in figure 5.9 is only included to show the trend more clearly.

The optimum solids concentration is also dependent on the size of the particles used. The above graph relates to sand with an average particles size of 300 μm. For experiments with larger particles a slightly higher solids concentration was used and the opposite for smaller particles. To ensure optimum conditions, this physical characteristic of the pulp was kept constant throughout all experiments (same as 80%

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point above). This optimum was very carefully obtained because even a few millilitres of water altered the pulp significantly.

5.3.3 Attrition Time

From figure 5.10, it can be seen that attrition time in excess of 30 minutes, do not significantly remove any more contaminant.

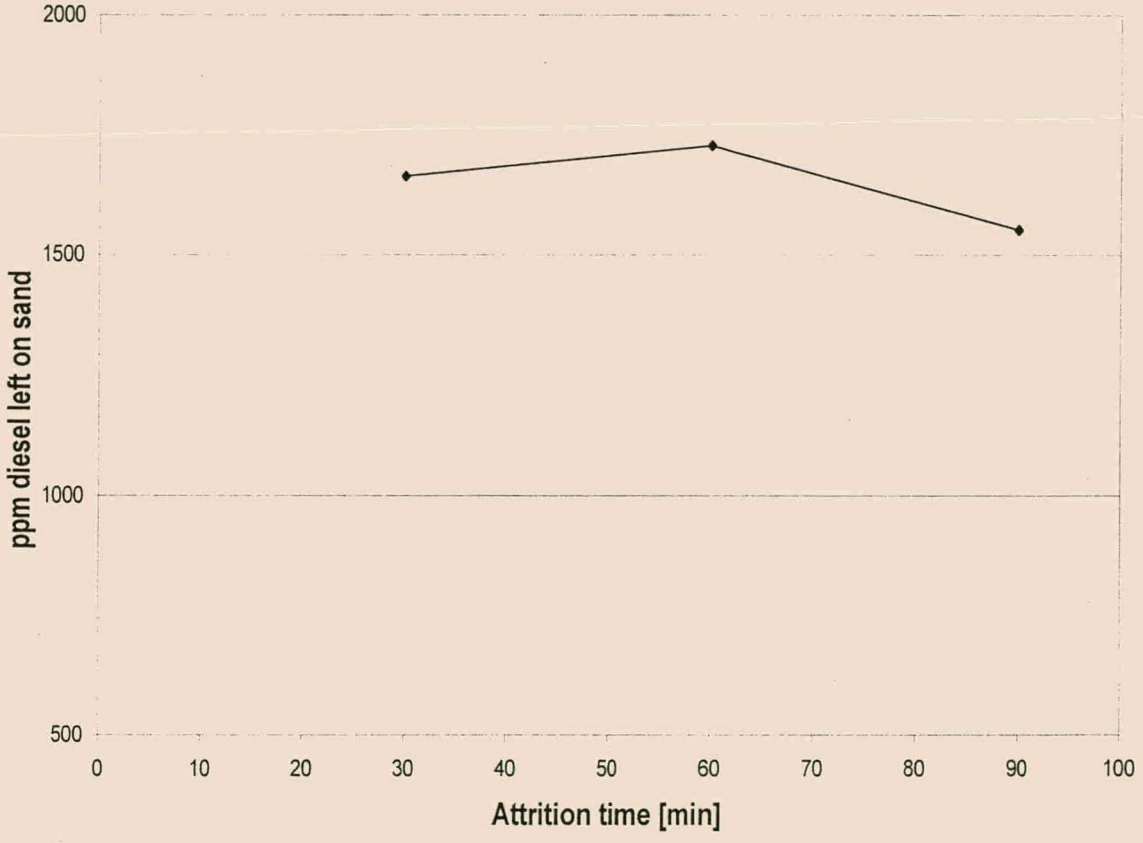

Figure 5.10. Influence of Attrition Time

No curve fitting was performed on the data, the line in figure 5.10 is only included to show the trend clearly.

The necessary attrition time is dependent on the effectiveness of the scrubbing and the strength of the bonds between the soil and the contaminant. In this case, the process seems to be working very well (and fast) for the system under consideration. If the bonds are of such a nature that the energy input from the scrubbing is less, the

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contaminant will not be removed. Likewise, if the interparticle motion is such that not all the particles experience the scrubbing, the contaminant will not be completely removed.

Finally, there is the ever-troubling phenomenon of hysteresis. It has been shown that the adsorption and desorption does not follow the same path and therefore not all of the contaminant can be removed. Unfortunately, this as yet cannot be explained.

5.3.4 Size Fraction

Four different samples of sand, differing only in size distribution, were again used. A very broad range particle size range was covered, from the very fine sand (42% -10 μm), to the fairly coarse sand (+ 500 μm) as well as a mixture of 75% 10 μm sand and 25% 500 μm sand, to represent a 'real' soil that corresponds to a sandy loam soil.

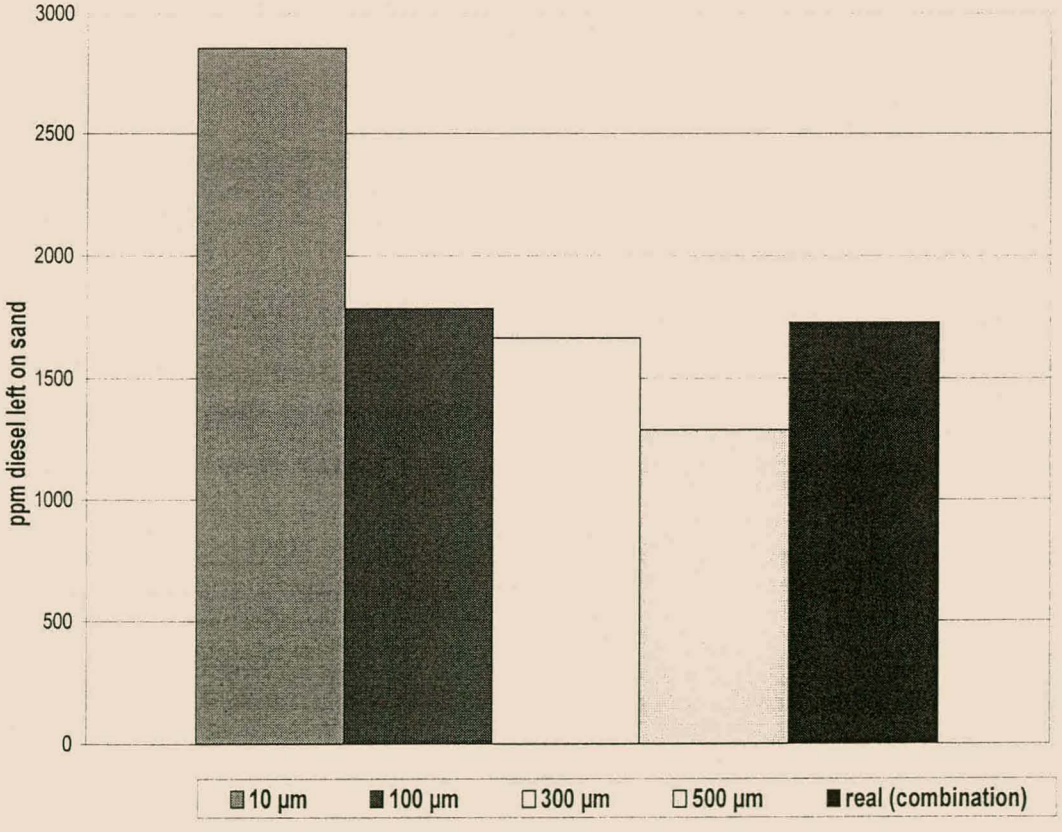

Figure 5.11. Influence of Particle Size

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In contrast to the poor results achieved with the jet, it seems that this technology is capable of handling fine particles and that almost any type of soil (clays excluded) could possible be effectively treated or pre-treated depending on the site and legislation.

As seen from figure 5.11, the larger the sand particles, the more effective the process of removing the contaminant (once again the values for the 100 μm and 300 μm sand lie close together). This was expected and can easily be explained if one considers the nature of the process and the differences in surface area per unit mass for the different types of sand. One can imagine that the finer the sand gets, the more surface area and thus adsorption sites there are available for the contaminant to bond to. In addition, the finer the sand, the lower the possibility that all the sites will encounter effective scrubbing.

Also interesting is to note that even for such a broad range of particle sizes, the upper and lower limits achieved lie fairly close together (between 1000 ppm and 3000 ppm). This proves the relative insensitivity and effectiveness of the process over this wide range. Remembering that size distribution is the most important factor when considering soil washing as a remediation option, it is promising to see this process being so effective over the entire range possible.

Looking at the 'real' soil, very good results were observed. It is expected that this value will be lower than that of the fine sand due to the amount of 500 μm sand present (dilution effect), but this alone cannot account for low level of contamination achieved. It thus seems that the coarser particles aid the attrition process by increasing the scrubbing on the fine particles beyond that previously attained alone and thus lowering the residual amount of diesel on the sand.

5.3.5 Stirrer Speed

The stirrer speed is an indication of external energy input into the system. Experiments were performed at three stirrer speeds up to a value of 600 rpm, the

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highest possible with the apparatus used. As expected the higher this energy input, the more efficient the process. A higher stirring speed causes the interparticle movement to be more violent, thus intensifying the scrubbing process. This effect is also particularly valuable for the smaller particle sizes. It is shown in figure 5.12, that for the smaller particle size (100 μm), the effect is more pronounced.

This can be explained that there are more particles and a greater surface area per mass for small particles. This means that the likelihood that a particular adsorption site will experience scrubbing decreases with a decreasing particle size. Now, when the stirring energy input increases, this causes more turbulence and more of these adsorption sites experience scrubbing. Thus, for the larger particles, a few more sites are cleaned but this number increases significantly as the particle sizes decrease. There is an optimum after which higher energy input would result in a negligible increase in cleaning, and the energy will be wasted. Again, the effect of hysteresis could also play an effect here.

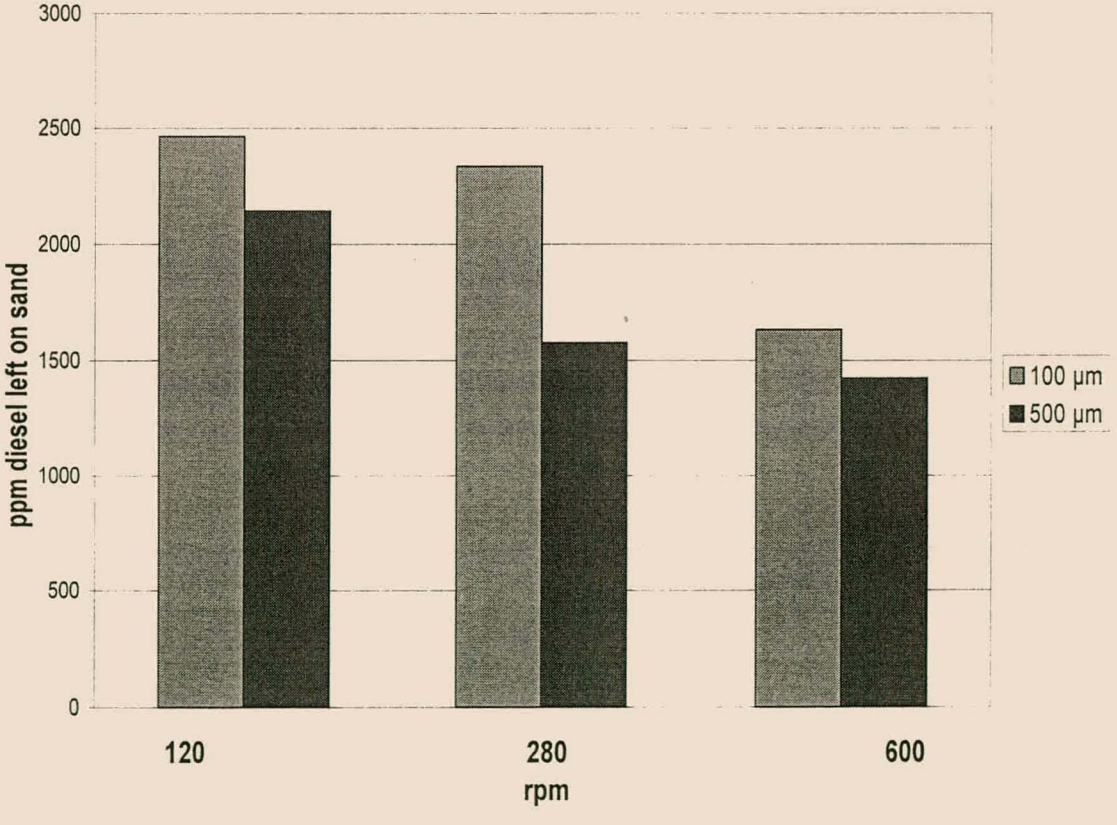

Figure 5.12. Influence of Stirrer Speed

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5.3.6 Number of Stages

In essence, the diesel is being transferred from the sand to the washwater. However, this is not a one-way process, as some of the removed diesel re-adsorbs. This is regulated by the concentration gradient in the slurry. It naturally leads to the fact that to remove the wash fluid and replace it with clean washing fluid, would remove some more of the contaminant.

This can be seen in figure 5.13, and two stages seem adequate to remove all the diesel that can be removed with this type of procedure. A decrease in diesel of 29% and 21% is achieved for the 100 μm and 500 μm sand, respectively. It is encouraging to see the huge increases in efficiency especially for the smaller particles and this should be kept in mind when designing a complete treatment system.

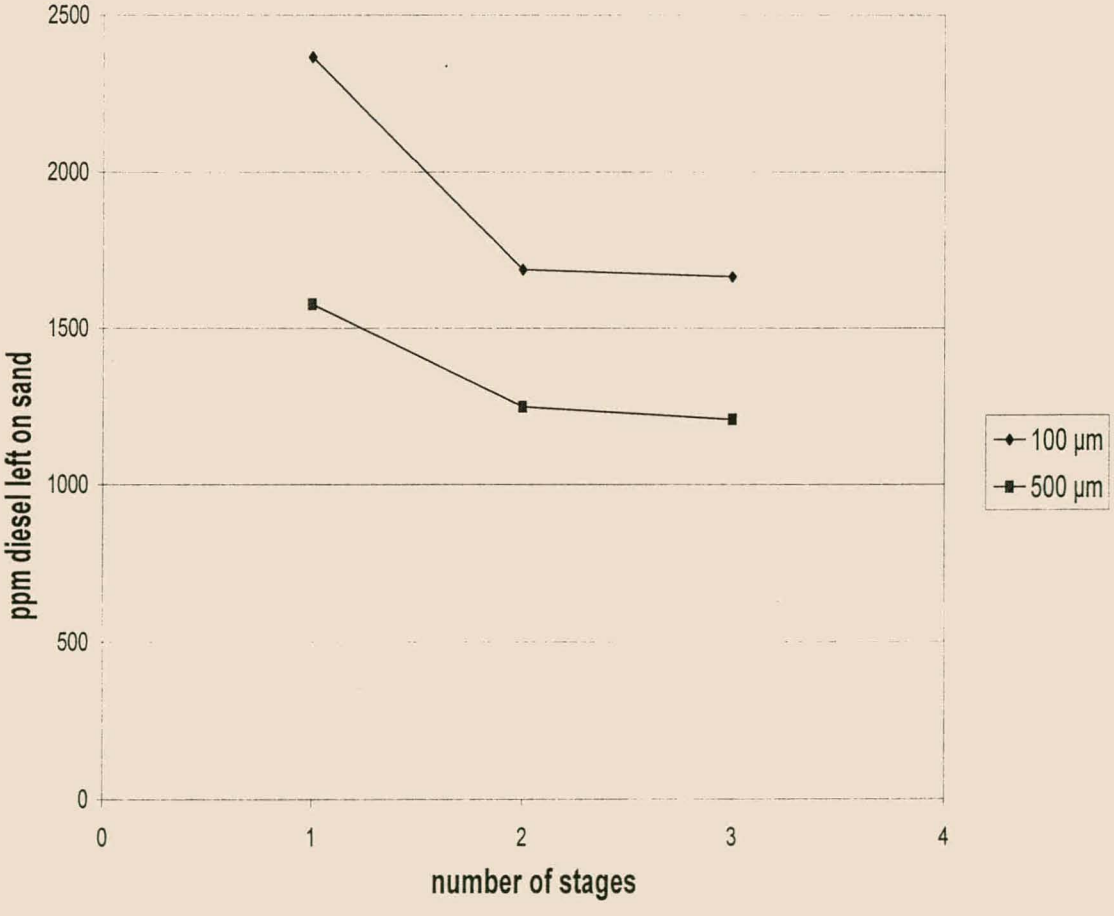

Figure 5.13. Multiple Attrition Stages

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5.3.7 Temperature

Just as stirring is a way of energy input into the system, so is temperature. An increase in temperature increases the solubility of the diesel in the water as well as enhancing the removal process. Figure 5.14 is concerned with only the influence of temperature and not of attrition. In the experiments, solids concentration of the slurry was kept so low (10%) that attrition would not have an influence. The stirring speed was kept at 280 rpm so that it can be compared to the attrition experiments done at this speed.

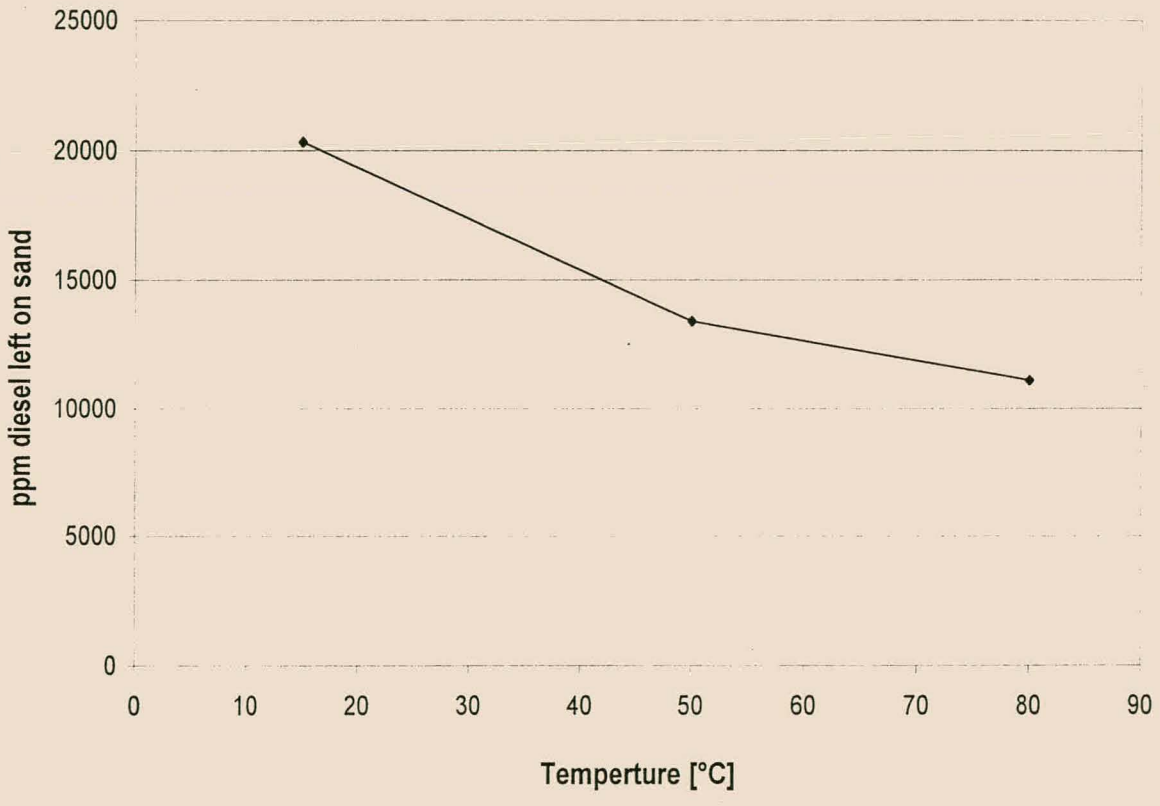

Figure 5.14. Temperature Influence

It is clear that even at ambient temperature a substantial amount (60%) of diesel is removed. When the temperature is raised to 50 °C, an additional 15% diesel is removed. A further temperature increase to 80 °C also removed more contaminant, but only 3% more and it therefore seems that an asymptotic value was reached, whereby further temperature increases would only be a waste of energy as well as complicating the operability of the process (harmful fumes). It is clear that an increase

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in temperature does enhance the removal process and that an optimum temperature exists for the system after which any further increases will not be beneficial.

5.3.8 Combining 2 stages with temperature

Using information obtained from the previous two sets of experiments, the combination of two stages and temperature were investigated. The first stage consists of a normal attrition stage after which the wash water was removed and replaced with clean water and the temperature of the slurry maintained at 50 °C for the second stage of attrition. The results are shown in figure 5.15 and compared to both normal single stage attrition and two-stage attrition.

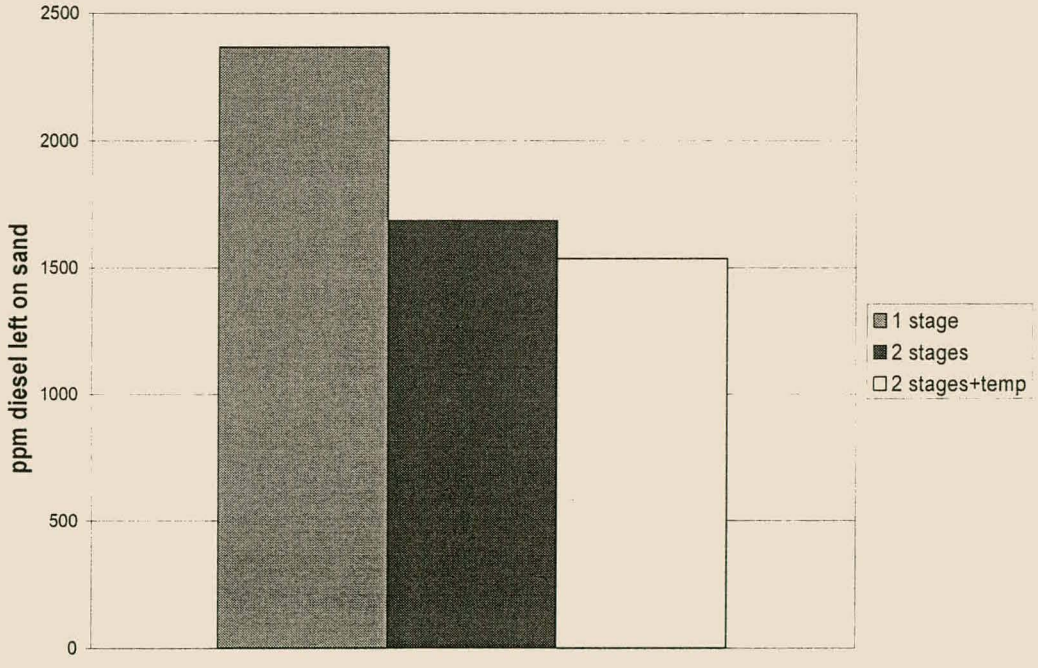

Figure 5.15. The effect of two stages and temperature

Figure 5.15 shows that a 9% improvement in diesel removal was attained by increasing the temperature. This is significant enough to merit the use of increased temperature in a complete treatment system.

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5.4 GC – Analyses

It was thought that because diesel is comprised of a large number of components, that some components might be more readily removed than others. The major components were found to be n-C11 to n-C22 and more than 75% of the mixture could be accounted for by the above mentioned species.

Together with the chromatograms, the area percentage contributions of all the species were obtained. Figure 5.16 shows the normalised percentage contributions of the major species for both the 'pure' diesel and the diesel extracted from the sand after the removal processes.

It can be seen that species smaller than n-C15 are being removed predominantly. This is very important to know when considering follow up treatment methods e.g. bioremediation. Sonochemistry can also be used to remove the residual diesel and Dr. D. Feng has shown that by using six stages in serie, it is possible to reduce the diesel contamination on 100 μm sand to 100 ppm (larger particles requiring less stages).

5.5 COST ESTIMATION FOR SSSA

It has been shown that the SSSA process is operationally simple and effective over the whole range of particle sizes studied. The main consideration however, will always be the cost effectiveness and a first estimation of major cost items is shown in Table 5.4.

Table 5.4 Cost Estimation of SSSA process

	[R/ton]
Excavation	2
Process Costs	
Electricity (20 kWh/ton)	7
Water (200L/ton)	0,4
Net Price	***9,4***

The above costs do not include solid liquid separation, but it will be minimal so that a first estimate of R10/ton can be made. Washwater treatment and other residuals management costs are also not included.

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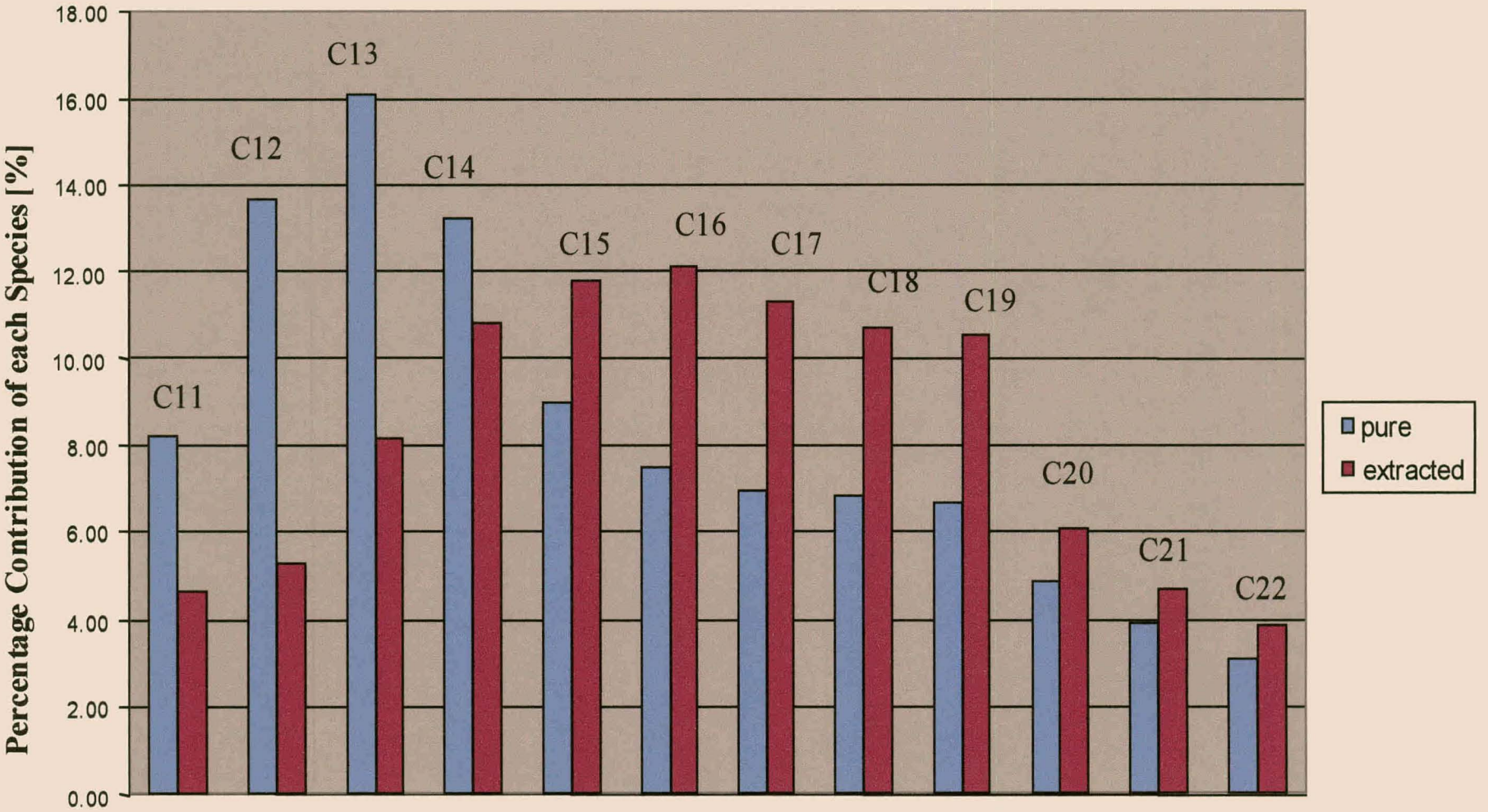

Figure 5.16. GC-Analyses of Pure and Extracted Diesel

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CHAPTER 6

SENSITIVITY ANALYSIS

STATISTICAL ACCURACY

Trends identified here are statistically valid, as statistical error bands are small enough, except for 6.1.4 where the values lie too close together. Trends identified there (6.1.4) are from an insight into the process and should be taken as such.

6.1 IMPINGING JET REACTOR

6.1.1 Jet Pressure

In figure 6.1, the sensitivity of the process to the jet stream pressure is shown. The process appears to be rather insensitive to this variable considering the small decrease (18%) in the amount of diesel left on sand when increasing the pressure by 200% from 10 MPa to 30 MPa. It is however, clear that a higher pressure does produce better results, but the total decrease is small as stated before.

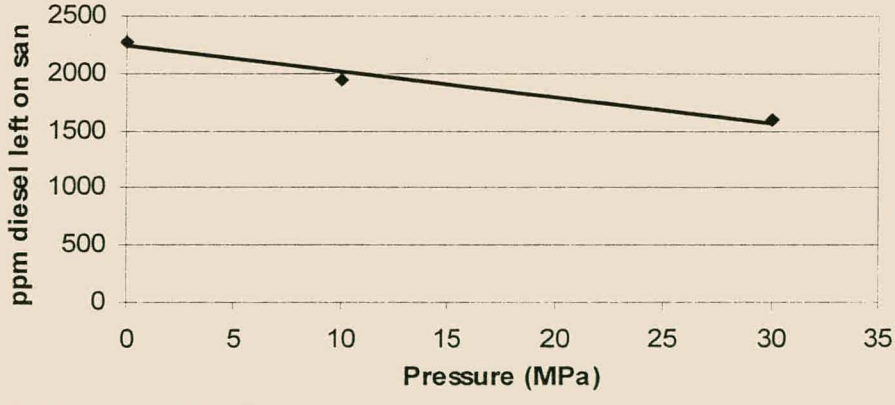

Figure 6.1 Influence of Jet Pressure

6.1.2 Slurry Flowrate

Figure 6.2 shows the sensitivity of the process to the slurry flowrate. The high and low values shown represent the highest and lowest values possible with the apparatus.

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The process is insensitive to this variable as can be seen from the small decrease (16%) in the amount of diesel left on sand when decreasing the slurry flowrate by 39% i.e. from 26 kg/min to 16 kg/min. Low slurry flowrates produce slightly better results but this also decreases throughput.

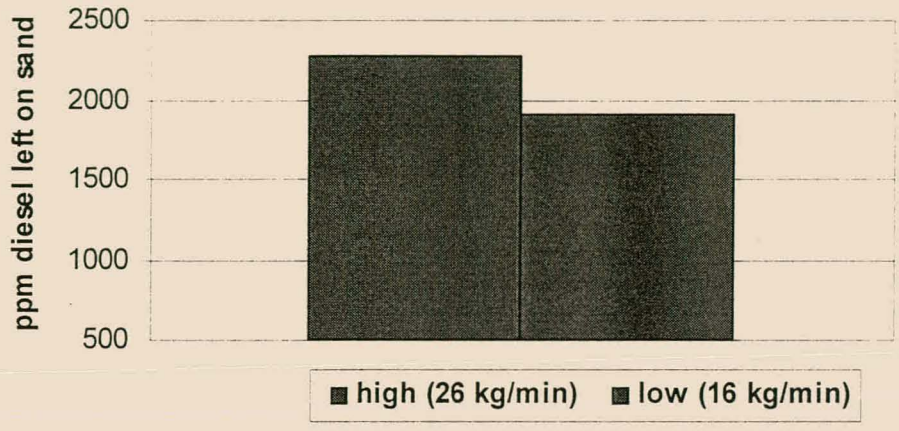

Figure 6.2 Influence of Slurry Flowrate

6.1.3 Size Fraction

Figure 6.3 shows the four samples of sand used and the sensitivity of the process to the particle sizes. For particle sizes 100 µm and bigger, the process seems very insensitive to the difference in particle sizes, and the trend is expected to continue to even larger particles, the only consideration then being the ability of the apparatus to handle larger particles.

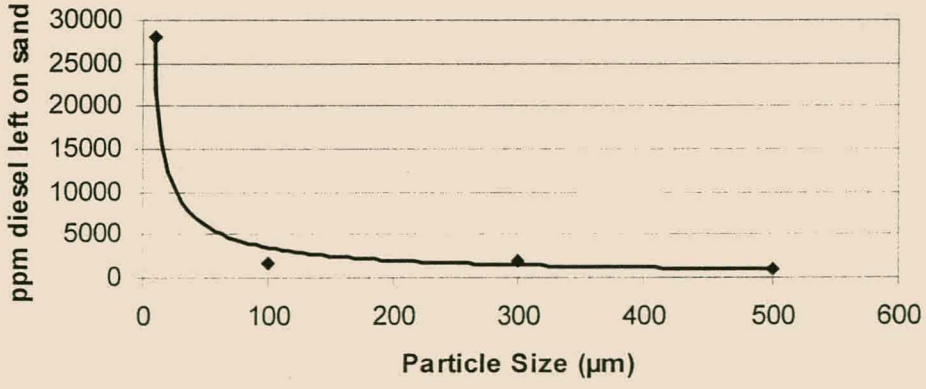

Figure 6.3 Influence of Particle Size

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For particles smaller than 100 μm however, the process becomes highly sensitive. A 10% increase in particle size from 10 μm results in a 27 % increase in efficiency and vice versa (decrease in the amount of diesel left on the sand). The finer the particles get the more sensitive the process until clay sized particles (-2 μm) are reached which cannot be handled by the apparatus.

6.1.4 Solids Concentration

Figure 6.4 shows the sensitivity of the process to the solids concentration of the slurry for the 100 μm sand. The best results are obtained at the lowest solids concentrations and the process is sensitive to this variable due to the competing cleaning mechanisms of jet washing and scrubbing as described in section 5.2.6.

Reducing the solids concentration from 15% to 10% decreases the diesel on the sand by 13% due to better contact with the jet. Increasing the solids concentration from 15% to 20% decreases diesel on the sand by 9% as interparticle scrubbing now plays an important role.

The smaller the particles the more sensitive the process to this variable and vice-versa.

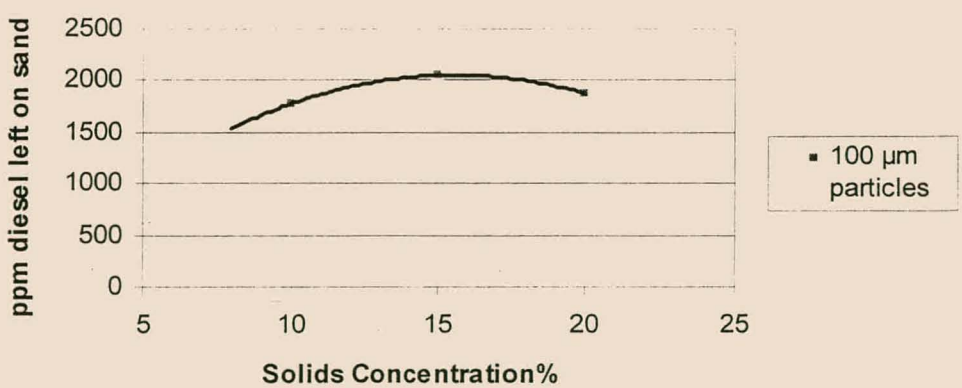

Figure 6.4 Influence of Solids Concentration

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6.2 SELECTIVE SOFT SELF ATTRITION

6.2.1 Size Fraction

Figure 6.5 shows the four samples of sand used and the sensitivity of the process to the particle sizes. Looking firstly at the 100 μm, 300 μm and 500 μm sands, the process seems insensitive to the difference in particle sizes covered and the trend is expected to continue to even larger particles, as was the case for the jet washing.

For particles smaller than 100 μm however, the process becomes more sensitive. Decreasing the particle size from 100 μm to 10 μm results in a 60 % decrease in efficiency (increase in the amount of diesel left on the sand). The finer the particles get, the more sensitive the process, until clay sized particles (-2 μm) are reached which cannot be handled by the apparatus as interparticle scrubbing will then be lost.

This relatively low sensitivity in comparison to the jet washing, means that SSSA is more suited to handle fine material and therefore a wider range of particle sizes.

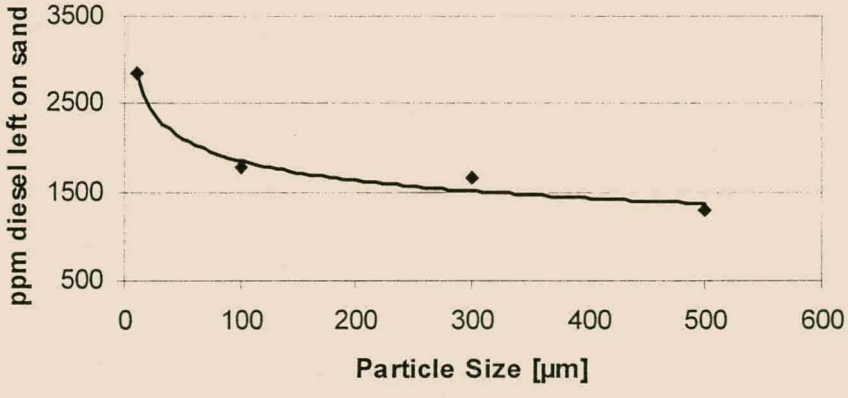

Figure 6.5 Influence of Particle Size

6.2.2 Solids Concentration

Figure 6.6 shows the sensitivity of the process to the solids concentration of the slurry. It can be seen from the figure that this variable is very important. Reducing the

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slurry concentration by 10% from the optimum (80% solids), results in a 27% reduction in efficiency (increase in amount of diesel left in sand) of the process. Increasing the solids concentration from 80% to 85% increases the amount of diesel on the sand by 53%. For solids concentrations lower than 70% the interparticle scrubbing is not being fully utilised and at solids concentrations higher than 85% the pulp is so dense that all interparticle scrubbing is lost and the slurry merely moves around the container as a unit.

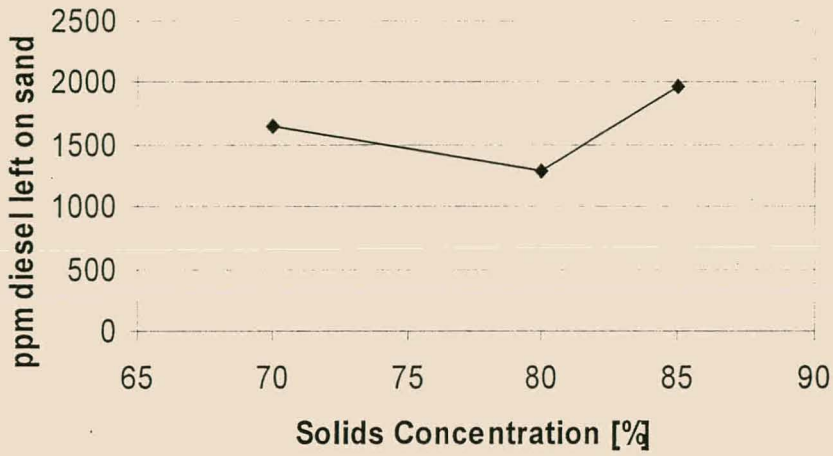

Figure 6.6 Influence of Solids Concentration

6.2.3 Attrition Time

The diesel is removed rapidly so that the process is insensitive to attrition time, 30 minutes being sufficient.

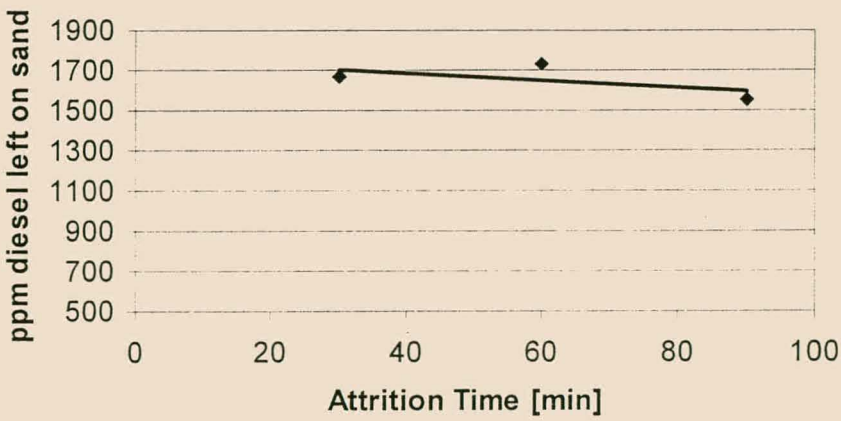

Figure 6.7 Influence of Attrition Time

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6.2.4 Stirrer Speed

This process is definitely sensitive to stirrer speed as can be seen from figure 6.8 and it is likely that higher stirring speeds will remove more diesel from the sand. Increasing the stirrer speed from 280 rpm to 600 rpm results in 30% more diesel being removed.

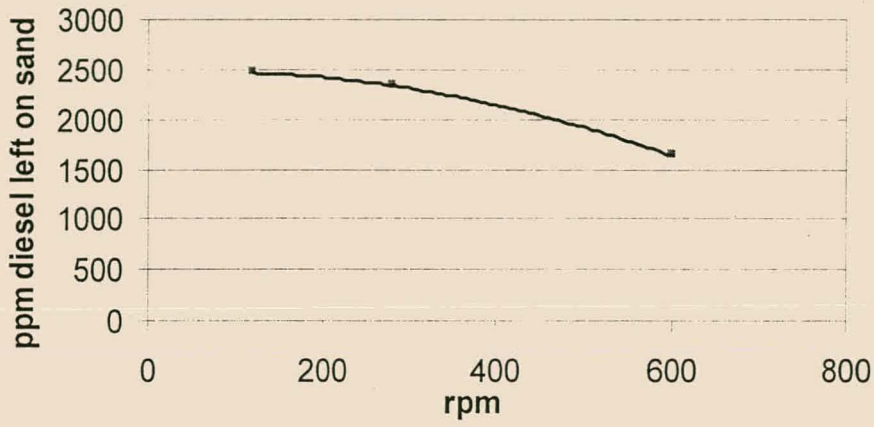

Figure 6.8 Influence of Stirrer Speed

6.2.5 Number of Stages

The process is sensitive to the amount of attrition stages used but only up to two stages. More stages do not remove any more diesel. 29% more diesel is removed by the second stage.

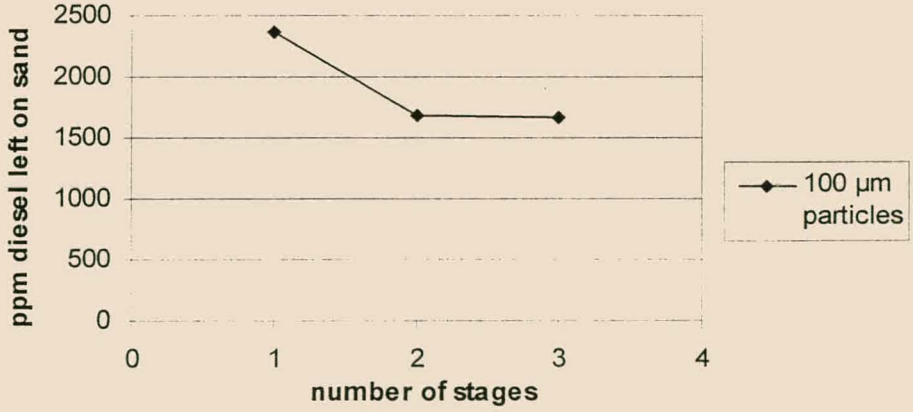

Figure 6.9 Multiple Attrition Stages

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6.2.6 Combining Two Stages with Temperature

Temperature does have a positive effect in that 9% more diesel is removed by heating the slurry to a temperature of 50 °C but the process is not markedly sensitive to this variable.

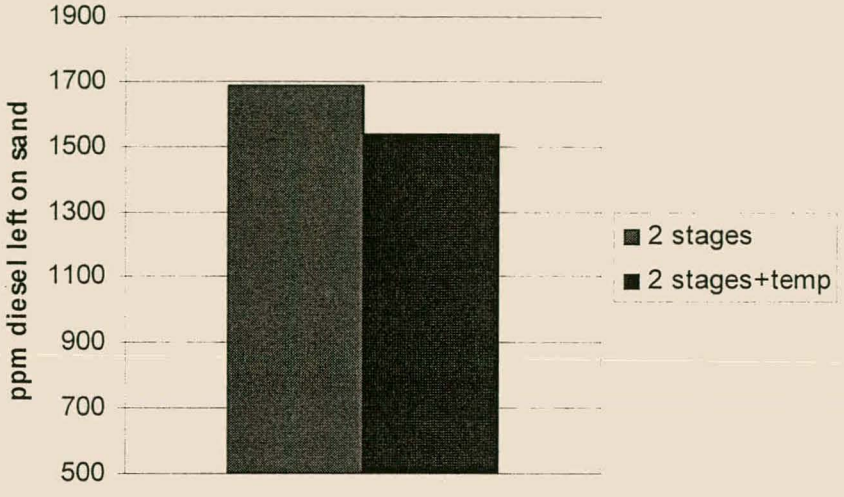

Figure 6.10 Influence of Temperature

6.3 SUMMARY OF CONCLUSIONS REACHED

6.3.1 Impinging Jet Reactor

- The process is insensitive to jet stream pressure and slurry flowrate.
- The process is highly sensitive to the particle size of the soil. Particles larger than 100 μm are cleaned effectively but smaller particles are not treated effectively.
- Solids concentration is an important variable as too high a solids concentration results in less effective jet washing. However, interparticle scrubbing then begins to play an important role.

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6.3.2 Selective Soft Self Attrition

- This process is also sensitive to particle sizes, but not as much as the jet washing process. Particles down to 10 μm are cleaned effectively. Smaller clay like particles may pose a problem, as the necessary interparticle scrubbing will be lost.
- The process is highly sensitive to solids concentration. Too low a solids concentration does not make full use of the interparticle scrubbing cleaning mechanism and too high a solids concentration results in no scrubbing at all as the pulp is merely moved around the container as a unit.
- Attrition time is not that important a variable, as diesel removal is fast and 30 minutes is sufficient.
- Stirrer speed is highly important and with an increase in stirring, the cleaning is more efficient.
- Using two stages in series makes a significant improvement in the residual diesel left on the sand, but more stages does not have any benefits.
- Temperature offers slightly better removal of the diesel but the process is not that sensitive to this variable.

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CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

The following important conclusions can be made from this research project, i.e.:

7.1 IMPINGING JET REACTORS

- The jet pressure does not have a major impact on the cleaning capacity of the apparatus. An increase from 10 MPa to 30 MPa removes only slightly more diesel (18%).

- A low slurry flowrate (16 kg/min) results in slightly better cleaning performance as contact with the jet stream is then a maximum, but the process is not particularly sensitive to this variable.

- Due to the continuous stirring and pumping of the slurry (when recycled), most of the diesel is removed before the sand is fed to the reactor. Only marginally better results are achieved when the jet is utilised.

- For the present reactor configuration, there exists a lower limit of particle sizes treatable and the process is extremely sensitive to this variable. Sandy soils (100 μm, 300 μm and 500 μm) are treated effectively and contamination levels are reduced to below 2000 ppm, but silts (10 μm, fine sand) are not being cleaned effectively by the jet.

- Adding course sand (500 μm sand) to the fine sand (10 μm sand) to represent a sandy loam soil (a more 'real' soil), did not improve the cleaning ability of the unit towards the fine fraction and thus, the unit is at present unable to treat fine particles.

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- The solids concentration of the slurry should be kept low to maximise the contact with the jet stream (10% solids). The process shows some sensitivity to this variable due to the competing washing mechanisms of jet stream washing and interparticle scrubbing at low (10%) and high (20%) solids concentrations, respectively.

7.2 SELECTIVE SOFT SELF ATTRITION

- Solids concentration of the slurry is an integral variable in the performance of this process and should be carefully maintained (around 80%).

- Removal of the diesel is rapid with this technology (30 minutes being sufficient).

- The process seems to be rather insensitive to particle size and reduces contamination levels to between 1000 ppm and 3000 ppm for all soils tested.

- The process will however, be very sensitive to finer particles (< 10 μm) that are in the clay region as the major washing technique, i.e. interparticle scrubbing, will then be lost.

- Adding larger particles as grinding agents (also more realistic soil composition) enhances the efficiency of the process for fine fractions and reduces contamination levels beyond that previously attained (now lower than 2000 ppm).

- Stirrer speed is an important variable and the higher the stirring speed, the better the cleaning of the sand.

- By removing and replacing the wash fluid with clean wash fluid for two stages of attrition, a significant amount more of the contaminant, is removed. More stages offer no improvement.

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- Increasing the temperature of the slurry (50 °C) aids in the removal of the diesel, but the process is not very sensitive to temperature over the range tested (0°C – 80°C).

7.3 GENERAL

- It is important to note the relevant legislation as applicable to hydrocarbon contaminated soil. This will aid the conclusions reached in showing what level of remediation was achieved in relation to that prescribed.

  For total petroleum hydrocarbons, three types of sites and their clean-up levels (mg/kg or ppm) have been defined in accordance to the risk posed to groundwater supplies, humans and the environment (Morris, 1996):

  ♦Low risk sites → 5000 ppm

  ♦Medium risk sites → 2500 ppm

  ♦High risk sites → 200 ppm

- Considering the values above, both processes are suitable to treat 'medium risk' sites as stand-alone units at present if the size distribution corresponds to that shown effective for each (clays have not been tested and the jet cannot treat silts).

- Both processes are also suitable as pre-treatment methods for bioremediation and will significantly reduce the total clean-up time of a contaminated site.

- The simplicity, ease of operation and wide effective particle size range makes the SSSA process more attractive than the Jet Washing at present.

- Most of the diesel is removed by stirring (as seen with jet reactor experiments). When the solids concentration is increased as with SSSA process, the diesel removal increases. The same occurs when the high-pressure water jet is used. The removal efficiency of the two processes being comparable for sandy soils.

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- The components lighter than C15 are predominantly removed.

7.4 RECOMMENDATIONS

- Different jet reactor configurations should be tested, as the energy of the jet stream is not being utilised fully at present, and fine fractions are not effectively in contact with the jet (this may be because the apparatus was initially designed for gold leaching purposes and only adapted for this study).

- Higher stirring speeds for attrition should be investigated, as this will improve removal of the diesel.

- The effect of using larger particles as a grinding agent should be further investigated to improve effectiveness of the SSSA process over the entire range.

- More realistic types of soil as well as different contaminants should be used to establish the effective applicable range of the processes.

- SSSA processes should be combined with bioremediation to establish a complete treatment process.

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REFERENCES

Alberts, C. J., 1996, 'The Immobilisation of Inorganic Pollutants in fly-ash and other Waste Components', *MSc(Eng)-Thesis*, University of Stellenbosch.

Anderson, William C., 1993, 'Innovative Site Remediation Technology', Volume 3, *Soil Washing/Soil Flushing*, Springer Verlag Berlin, pp 1.1 – 7.2.

Bezuidenhout, S., 1998, 'Jet Loging', *Laboratory Project*, University of Stellenbosch, p1 – 41.

Botes, F. G., 1995, 'The development and modelling of jet reactors', *MSc(Eng)-Thesis*, University of Stellenbosch, pp 1- 34.

Boulding, J. R., 1996, 'Soil washing treatment', *EPA environmental engineering sourcebook*, Chapter 17, pp 233 - 245.

Bruckmann, C. G. & Mandersloot, W. G. B., 1988, 'Writing informative reports on investigations in science and engineering', CSIR, pp 1 - 37.

Cacciatore D. A. & Mc Neil M. A., 1995, 'Principles of Bioremediation', *Biocycle*, p61.

Couillard, D., Tran, F. T. & Tyagi, R. D., 1991, 'Process for the In Situ Restoration of Oil-contaminated Soils', *Journal of Environmental Management*, 32, pp 19-34.

Demque D. E., Biggar K. W., and Heroux, J. A., 1997, 'Land Treatment of diesel contaminated sand' Canadian Geotechnical Journal, Volume 34, pp 421 – 431.

Dennis, R. M., Dworkin, D. & Zupko, A. J., 1994, 'Soil Washing Processes for Site Remediation', in *Remediation of Hazardous Waste Contaminated Soils*, Chapter 31, D.L. Wise, D. J. Trantolo, pp 745 – 777.

Stellenbosch University https://scholar.sun.ac.za

Dineen, D., 1991, 'Remediation options for diesel contaminated soil', *Hydrocarbon Contaminated Soils*, Volume 1, pp 181 – 191.

Ferguson, Colin R., 1986, 'Internal Combustion Engines', *Applied Thermosciencs*, John Wiley & Sons, pp 433 - 451.

Flowers, T. H., Pulford, I. D. & Duncan, H. J., 1984, 'Studies on the Breakdown of Oil in Soil', *Environmental Pollution* (Series B), 8, pp 71-82.

Francis, W., 1965, 'Fuels and Fuel Technology, A Summarised Manual', Volume 1, Pergamon Press, pp 209 – 348.

Jones, T. M., Ghassemi, A., 1994, 'Modern In-Field Process Systems – Case Study: Soil Washing', in *Remediation of Hazardous Waste Contaminated Soils*, Chapter 30, D.L. Wise, D. J. Trantolo, pp 719 – 743.

Martin, I. D. & Bardos, P., 1994, 'Recent Developments in Contaminated Land Treatment Technology', *Chemistry and Industry London*, no 11, pp 411 – 413.

McGill, W. B. & Rowell, M. J., 1980, 'Determination of Oil Content of Oil Contaminated Soil', *The Science of the Total Environment*, 14, pp 245-253.

Morris, R., 1996, 'Rational and practical approach required when selecting standards for hydrocarbon contaminated site assessment and remediation', *Water, sewage and effluent*, Volume 16, Issue 1, pp 57-61.

Ryan, W., 1968, 'Non-ferrous Extractive Metallurgy in the United Kingdom', Kynoch Press, Birmingham, p1.

Sharp, K. H., 1993, 'Selective Soft Self Attrition Gold Dissolution', *Provisional Patent application* NR: 93/9645, 34 pages.

Stellenbosch University https://scholar.sun.ac.za

Tamir, A., 1994, 'Impinging-Stream Reactors, Fundamentals and Applications', Elserivier Science B.V., pp. 1 - 39.

Van Zyl, H. D., 1998, 'Ex-Situ Bioremediation of Hydrocarbon Contaminated Soil Using The Soil Pile Technique', *MSc(Eng)-Thesis*, University of Stellenbosch, pp 1 - 124.

Van Zyl, F. J., 1995, 'The Selective Soft Self Attrition of gold ores', *Laboratory Project*, University of Stellenbosch, pp 1 - 50.

Van Zyl. R. L., 1997, 'The Immobilisation of heavy metal ions in metallurgical waste', *MSc(Eng)-Thesis*, University of Stellenbosch.

Wood, P. A., 1997, 'Contaminated Land and its Reclamation', *Issues in Environmental Science and Technology,* Volume 7, R. E. Hester, R. M. Harrison, The Royal Society of Chemistry, pp 47 – 71.

Yaron, B., Calvet, R., Prost, R., 1996, 'Soil Pollution, Processes and Dynamics', Springer Verlag Berlin Heidelberg, p 47.

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APPENDIX A

ORIGINAL RESULTS

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A1: Jet Reactor

All jet reactor runs were done as follows: 30 seconds jet only
30 seconds both jet and slurry
60 seconds jet only

	Experiment		1a	1b	average
goal :	low jet flow	Product [kg]	12.2	12.0	
		Sand [kg]	0.9	0.9	
Tipe of sand:	300 um	Jet [kg]	3.6	3.6	
Jet pressure:	10 MPa	Slurry [kg]	8.6	8.4	
Jet flowrate:	1.8 l/min	SC [%]	10.5	10.7	10.6
	diesel left after evaporation [g]:		0.0122	0.0121	
	concentration diesel left on sand [ppm]:		1952	1936	1944

	Experiment		2a	2b	average
goal :	high jet flow	Product [kg]	18.0	18.1	
		Sand [kg]	1.1	1.0	
Tipe of sand:	300 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	11.8	11.9	
Jet flowrate:	3.1 l/min	SC [%]	9.3	8.4	8.9
	diesel left after evaporation [g]:		0.0098	0.0101	
	concentration diesel left on sand [ppm]:		1568	1616	1592

	Experiment		3a	3b	average
goal :	high slurry flow	Product [kg]	20.0	18.2	
		Sand [kg]	1.4	1.1	
Tipe of sand:	300 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	13.8	12.0	
Jet flowrate:	3.1 l/min	SC [%]	10.1	9.2	9.7
	diesel left after evaporation [g]:		0.0157	0.0127	
	concentration diesel left on sand [ppm]:		2512	2032	2272

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Experiment			4a	4b	
					average
goal :	low slurry flow	Product [kg]	17.6	17.2	
		Sand [kg]	1.0	1.0	
Tipe of sand:	300 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	11.4	11.0	
Jet flowrate:	3.1 l/min	SC [%]	8.8	9.1	8.9
	diesel left after evaporation [g]:		0.0116	0.0123	
	concentration diesel left on sand [ppm]:		1856	1968	1912

Experiment			5a	5b	
					average
goal :	15% SC	Product [kg]	19.6	17.4	
		Sand [kg]	2.0	1.7	
Tipe of sand:	300 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	13.4	11.2	
Jet flowrate:	3.1 l/min	SC [%]	14.9	15.2	15.1
	diesel left after evaporation [g]:		0.0207	0.0178	
	concentration diesel left on sand [ppm]:		3312	2848	3080

Experiment			6a	6b	
					average
goal :	20% SC	Product [kg]	15.3	18.8	
		Sand [kg]	1.9	2.6	
Tipe of sand:	300 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	9.1	12.6	
Jet flowrate:	3.1 l/min	SC [%]	20.9	20.6	20.8
	diesel left after evaporation [g]:		0.0154	0.0178	
	concentration diesel left on sand [ppm]:		2464	2848	2656

Experiment			7a	7b	
					average
goal :	5% SC	Product [kg]	17.9	16.9	
		Sand [kg]	0.9	0.9	
Tipe of sand:	500 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	11.7	10.7	
Jet flowrate:	3.1 l/min	SC [%]	7.7	8.4	8.1
	diesel left after evaporation [g]:		0.0073	0.0071	
	concentration diesel left on sand [ppm]:		1168	1136	1152

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	Experiment		8a	8b	average
goal :	10% SC	Product [kg]	17.2	14.4	
		Sand [kg]	1.0	0.8	
Tipe of sand:	500 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	11.0	8.2	
Jet flowrate:	3.1 l/min	SC [%]	9.1	9.1	9.1
	diesel left after evaporation [g]:		0.0066	0.0067	
	concentration diesel left on sand [ppm]:		1056	1072	1064

	Experiment		9a	9b	average
goal :	15% SC	Product [kg]	13.6	16.4	
		Sand [kg]	1.0	1.5	
Tipe of sand:	500 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	7.4	10.2	
Jet flowrate:	3.1 l/min	SC [%]	13.5	14.7	14.1
	diesel left after evaporation [g]:		0.0057	0.0068	
	concentration diesel left on sand [ppm]:		912	1088	1000

	Experiment		10a	10b	average
goal :	10% SC	Product [kg]	18.0	16.6	
		Sand [kg]	1.3	1.0	
Tipe of sand:	100 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	11.8	10.4	
Jet flowrate:	3.1 l/min	SC [%]	11.0	9.6	10.3
	diesel left after evaporation [g]:		0.0117	0.0105	
	concentration diesel left on sand [ppm]:		1872	1680	1776

	Experiment		11a	11b	average
goal :	15% SC	Product [kg]	18.6	18.0	
		Sand [kg]	1.7	1.4	
Tipe of sand:	100 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	12.4	11.8	
Jet flowrate:	3.1 l/min	SC [%]	13.7	11.9	12.8
	diesel left after evaporation [g]:		0.013	0.0126	
	concentration diesel left on sand [ppm]:		2080	2016	2048

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	Experiment		12a	12b	average
goal :	20% SC	Product [kg]	15.7	15.7	
		Sand [kg]	1.8	1.9	
Tipe of sand:	100 um	Jet [kg]	6.2	6.2	
Jet pressure:	30 MPa	Slurry [kg]	9.5	9.5	
Jet flowrate:	3.1 l/min	SC [%]	18.9	19.5	19.2
	diesel left after evaporation [g]:		0.0124	0.011	
	concentration diesel left on sand [ppm]:		1984	1760	1872

	Experiment		13a	13b	average
goal :	20% SC	Product [kg]			
		Sand [kg]			
Tipe of sand:	fine	Jet [kg]			
Jet pressure:	30 MPa	Slurry [kg]			
Jet flowrate:	3.1 l/min	SC [%]			
	diesel left after evaporation [g]:		0.1537	0.1971	
	concentration diesel left on sand [ppm]:		24592	31536	28064

	Experiment		13a	13b	average
goal :	real soil	Product [kg]			
		Sand [kg]			
Tipe of sand:	75% fine, 25% 500µm	Jet [kg]			
Jet pressure:	30 MPa	Slurry [kg]			
Jet flowrate:	3.1 l/min	SC [%]			
	diesel left after evaporation [g]:		0.1512	0.1334	
	concentration diesel left on sand [ppm]:		24192	21344	22768

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A2: SSSA

All experiments were repeated at least twice, the two accepted are shown.

Experiment		1a	1b	average
goal:	70% SC			
Tipe of sand:	300 um			
Stirrer speed:	600 rpm			
Attrition time:	30 min			
	diesel left after evaporation [g]:	0.0098	0.0109	
	concentration diesel left on sand [ppm]:	1568	1744	1656

Experiment		2a	2b	average
goal:	80% SC			
Tipe of sand:	300 um			
Stirrer speed:	600 rpm			
Attrition time:	30 min			
	diesel left after evaporation [g]:	0.0084	0.0078	
	concentration diesel left on sand [ppm]:	1344	1248	1296

Experiment		3a	3b	average
goal:	85% SC			
Tipe of sand:	300 um			
Stirrer speed:	600 rpm			
Attrition time:	30 min			
	diesel left after evaporation [g]:	0.0139	0.0108	
	concentration diesel left on sand [ppm]:	2224	1728	1976

Experiment		4a	4b	average
goal:	30 min attrition			
Tipe of sand:	300 um			
Stirrer speed:	600 rpm			
SC :	80%			
	diesel left after evaporation [g]:	0.0096	0.0112	
	concentration diesel left on sand [ppm]:	1536	1792	1664

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Experiment	5a	5b	average
goal: 60 min attrition			
Tipe of sand: 300 um			
Stirrer speed: 600 rpm			
SC : 80%			
diesel left after evaporation [g]:	0.0112	0.0104	
concentration diesel left on sand [ppm]:	1792	1664	1728

Experiment	6a	6b	average
goal: 90 min attrition			
Tipe of sand: 300 um			
Stirrer speed: 600 rpm			
SC : 80%			
diesel left after evaporation [g]:	0.0093	0.0101	
concentration diesel left on sand [ppm]:	1488	1616	1552

Experiment	7a	7b	average
goal: 100 um sand			
Attrition time: 30 min			
Stirrer speed: 600 rpm			
SC : 80%			
diesel left after evaporation [g]:	0.0102	0.0121	
concentration diesel left on sand [ppm]:	1632	1936	1784

Experiment	8a	8b	average
goal: 500 um sand			
Attrition time: 30 min			
Stirrer speed: 600 rpm			
SC : 80%			
diesel left after evaporation [g]:	0.0089	0.0072	
concentration diesel left on sand [ppm]:	1424	1152	1288

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Experiment		9a	9b	average
goal:	fine sand			
Attrition time:	30 min			
Stirrer speed:	600 rpm			
SC :	80%			
	diesel left after evaporation [g]:	0.0195	0.0162	
	concentration diesel left on sand [ppm]:	3120	2592	2856

Experiment		10a	10b	average
goal:	280 rpm			
Tipe of sand:	300 um			
Attrition time:	30 min			
SC :	80%			
	diesel left after evaporation [g]:	0.0167	0.018	
	concentration diesel left on sand [ppm]:	2676	2880	2778

Experiment		11a	11b	average
goal:	280 rpm			
Tipe of sand:	100 um			
Attrition time:	30 min			
SC :	80%			
	diesel left after evaporation [g]:	0.0132	0.016	
	concentration diesel left on sand [ppm]:	2112	2560	2336

Experiment		12a	12b	average
goal:	280 rpm			
Tipe of sand:	500 um			
Attrition time:	30 min			
SC :	80%			
	diesel left after evaporation [g]:	0.0098	0.0099	
	concentration diesel left on sand [ppm]:	1568	1584	1576

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Experiment		13a	13b	average
goal:	120 rpm			
Tipe of sand:	100 um			
Attrition time:	30 min			
SC :	80%			
	diesel left after evaporation [g]:	0.015	0.0158	
	concentration diesel left on sand [ppm]:	2400	2528	2464

Experiment		14a	14b	average
goal:	120 rpm			
Tipe of sand:	500 um			
Attrition time:	30 min			
SC :	80%			
	diesel left after evaporation [g]:	0.0142	0.0126	
	concentration diesel left on sand [ppm]:	2272	2016	2144

Experiment		15a	15b	average
goal:	2 stages			
Tipe of sand:	500 um			
Attrition time:	30 min/30 min			
SC :	80%			
	diesel left after evaporation [g]:	0.0076	0.008	
	concentration diesel left on sand [ppm]:	1216	1280	1248

Experiment		16a	16b	average
goal:	3 stages			
Tipe of sand:	500 um			
Attrition time:	30 min/30 min/30 min			
SC :	80%			
	diesel left after evaporation [g]:	0.0077	0.0074	
	concentration diesel left on sand [ppm]:	1232	1184	1208

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Experiment		17a	17b	average
goal:	2 stages			
Tipe of sand:	100 um			
Attrition time:	30 min/30 min			
SC :	80%			
	diesel left after evaporation [g]:	0.0109	0.0102	
	concentration diesel left on sand [ppm]:	1744	1632	1688

Experiment		18a	18b	average
goal:	3 stages			
Tipe of sand:	100 um			
Attrition time:	30 min/30 min/30 min			
SC :	80%			
	diesel left after evaporation [g]:	0.0105	0.0103	
	concentration diesel left on sand [ppm]:	1680	1648	1664

Experiment		19a	19b	average
goal:	real soil			
Tipe of sand:	75% fine, 25% 500 um			
Stirrer speed:	600 rpm			
SC :	80%			
	diesel left after evaporation [g]:	0.0097	0.0119	
	concentration diesel left on sand [ppm]:	1552	1904	1728

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A3: Temperature Influence

Experiment		1a	1b	average
goal:	15 C			
Tipe of sand:	100 um			
Stirrer speed:	280 rpm			
Attrition time:	30 min			
SC :	10%			
	diesel left after evaporation [g]:	0.1326	0.1215	
	concentration diesel left on sand [ppm]:	21216	19440	20328

Experiment		2a	2b	average
goal:	50 C			
Tipe of sand:	100 um			
Stirrer speed:	280 rpm			
Attrition time:	30 min			
SC :	10%			
	diesel left after evaporation [g]:	0.0909	0.0767	
	concentration diesel left on sand [ppm]:	14544	12272	13408

Experiment		3a	3b	average
goal:	80 C			
Tipe of sand:	100 um			
Stirrer speed:	280 rpm			
Attrition time:	30 min			
SC :	10%			
	diesel left after evaporation [g]:	0.0655	0.0733	
	concentration diesel left on sand [ppm]:	10480	11728	11104

Experiment		4a	4b	average
goal:	2 stages and 50 C			
Tipe of sand:	100 um			
Stirrer speed:	280 rpm			
Attrition time:	30 min			
SC :	80%			
	diesel left after evaporation [g]:	0.0087	0.0105	
	concentration diesel left on sand [ppm]:	1392	1680	1536

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A4: Analytical Experiments

Pure diesel evaporation

	time [days]	mass [g]	diesel	% lost
empty container		20.04		
day 0	0	25.78	5.75	0
	0.5	24.78	4.74	17
day 1	1	23.88	3.84	33
	1.5	23.74	3.71	36
day 2	2	23.49	3.45	40
day 3	3	23.45	3.41	41
	3.5	23.42	3.38	41
day 4	4	23.29	3.25	43
	4.5	23.28	3.25	44
day 5	5	23.26	3.22	44
day 6	6	23.25	3.21	44

Contaminated Sand Evaporation

container + sand	282.4 g
add diesel	287.8 g
thus diesel	5.4 g

days	mass [g]	mass diesel [g]	% lost
1	287.3	5.4	0
2	286.9	4.9	9
3	286.1	4.5	17
6	285.5	3.7	31
8	285.5	3.1	43
9	285.3	2.9	46
10	285.2	2.8	48
11	285.2	2.8	48
12	285.2	2.8	48

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MCl evaporation

Two standards were made up by mixing diesel with MCl in a 100ml volumetric flask :

	Std 1	Std 2
diesel [g]	1.7555	4.4856

The important factors were: with/without a lid
with/without the fan on in the fumehood

Standard 1

Mass of diesel left after evaporation (1.7555g = no diesel losses)

	with fan	without fan
with lid	1.4752g	1.7028g
without lid	0.936g	

Standard 2

Mass of diesel left after evaporation (4.4856g = no diesel losses)

	with fan	without fan
with lid	4.1328g	4.4060g
without lid		3.3812g

Soxhlet Extraction and Evaporation

Three standards were made up by mixing sand and diesel:

	Std 1	Std 2	Std 3
sand [g]	199.8	199	198
plus diesel [g]	0.2	1	2
total [g]	200	200	200
% diesel	0.1	0.5	1
ppm	1000	5000	10000

After Extraction and Evaporation (50g sand sample) :

	mass of diesel left [g]	ave [g]
Std 1	0.0448	
	0.0440	0.0444
Std 2	0.2248	
	0.2326	0.2287
Std 3	0.4288	
	0.4316	0.4302

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A5: GC - Analyses

The area percentage contributions, as well as the normalised values, of the major identified species.

species	pure [%]		extracted [%]	
C11	6.26	8.20	3.40	4.65
C12	10.46	13.68	3.86	5.28
C13	12.26	16.05	5.94	8.13
C14	10.09	13.21	7.90	10.81
C15	6.88	9.00	8.64	11.82
C16	5.73	7.51	8.87	12.14
C17	5.30	6.93	8.26	11.30
C18	5.23	6.84	7.81	10.69
C19	5.10	6.67	7.69	10.53
C20	3.72	4.87	4.44	6.08
C21	3.01	3.94	3.45	4.73
C22	2.37	3.10	2.80	3.84
	76.40	***100.00***	**73.05**	***100.00***

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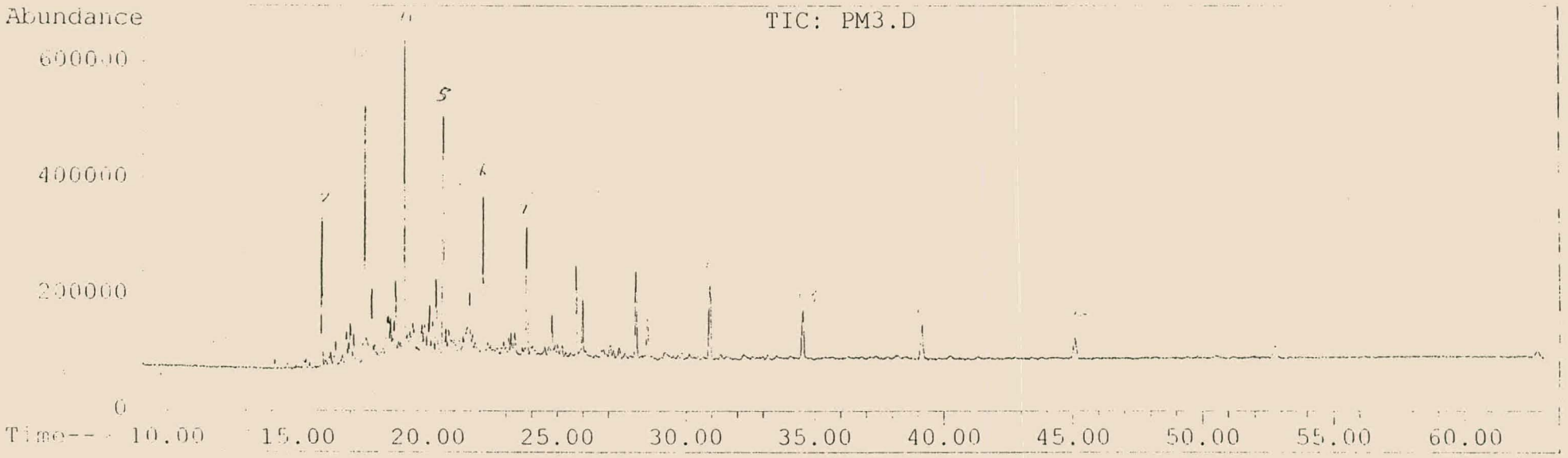
Operator :
Acquired : 3 Jun 99 2:10 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: skoon diesel
Misc Info :
Vial Number: 1



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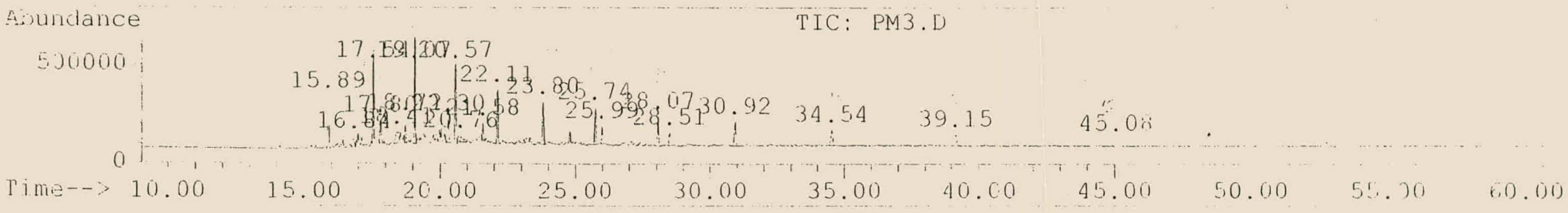
Area Percent Report -- Sorted by Signal

Information from Data File:
File : C:\HPCHEM\1\DATA\PM3.D
Operator :
Acquired : 3 Jun 99 2:10 pm using AcqMethod PIETER
Sample Name: skoon diesel
Misc Info :
Vial Number: 1
CurrentMeth: C:\HPCHEM\1\METHODS\HANLIE.M



Retention Time	Area	Area %	Ratio %	Type	Width
Total Ion Chromatogram					
15.889	740566	6.262	51.079	rBV	0.174
16.839	283336	2.396	19.542	rBV	0.165
17.544	1236560	10.455	85.288	rVV	0.101
17.801	400657	3.388	27.634	rBV	0.147
18.406	270545	2.287	18.660	rBV	0.128
18.717	323264	2.733	22.296	rVB	0.101

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Area Percent Report -- Sorted by Signal

Information from Data File:
File : C:\HPCHEM\1\DATA\PM3.D
Operator :
Acquired : 3 Jun 99 2:10 pm using AcqMethod PIETER
Sample Name: skoon diesel
Misc Info :
Vial Number: 1
CurrentMeth: C:\HPCHEM\1\METHODS\HANLIE.M

Retention Time	Area	Area %	Ratio %	Type	Width
19.066	1449858	12.259	100.000	rBV	0.110
20.296	354702	2.999	24.465	rVB	0.129
20.572	1193407	10.090	82.312	rBV	0.147
20.764	225844	1.910	15.577	rBV	0.248
21.582	323142	2.732	22.288	rVB	0.129
22.115	813548	6.879	56.112	rBV	0.184
23.804	678124	5.734	46.772	rVB	0.165
25.739	626291	5.295	43.197	rBV	0.138
25.986	324464	2.743	22.379	rVB	0.128
28.066	618316	5.228	42.647	rVB	0.220
28.506	285471	2.414	19.690	rVB	0.174
30.922	602749	5.096	41.573	rVB	0.229
34.545	440143	3.721	30.358	rVB	0.265
39.152	355838	3.009	24.543	rBV	0.220
45.082	280328	2.370	19.335	rVB	0.247

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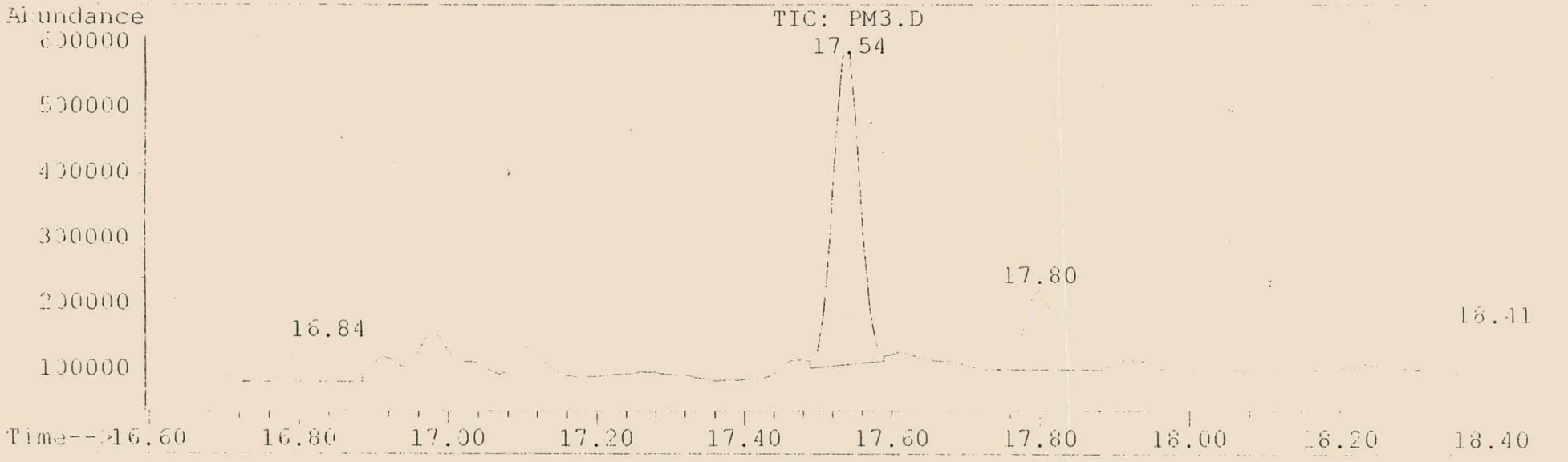
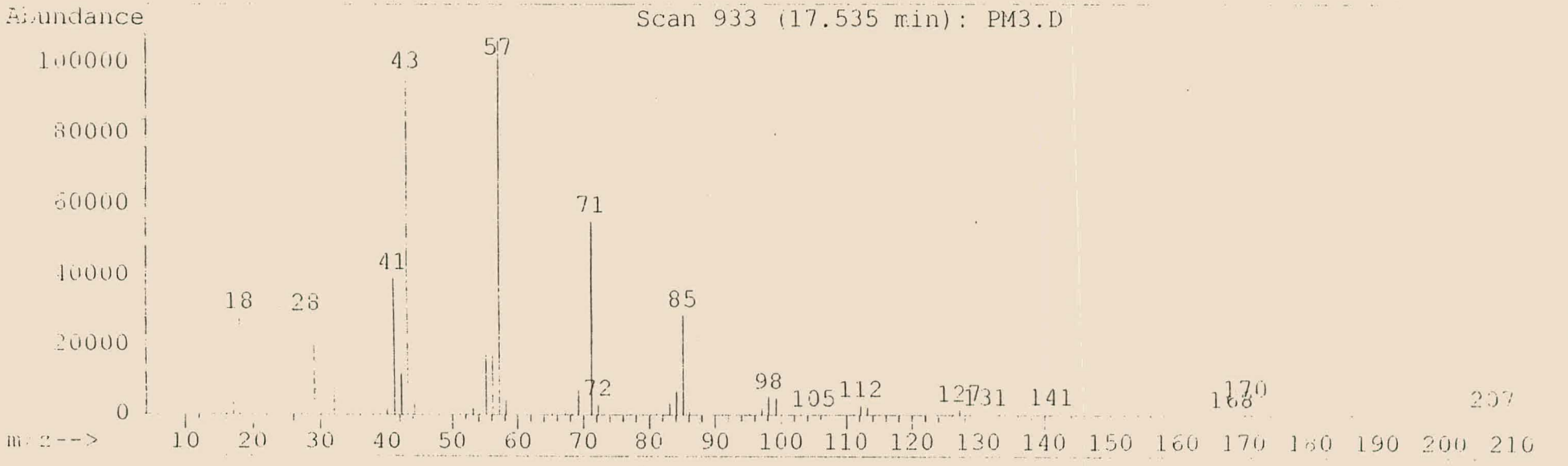
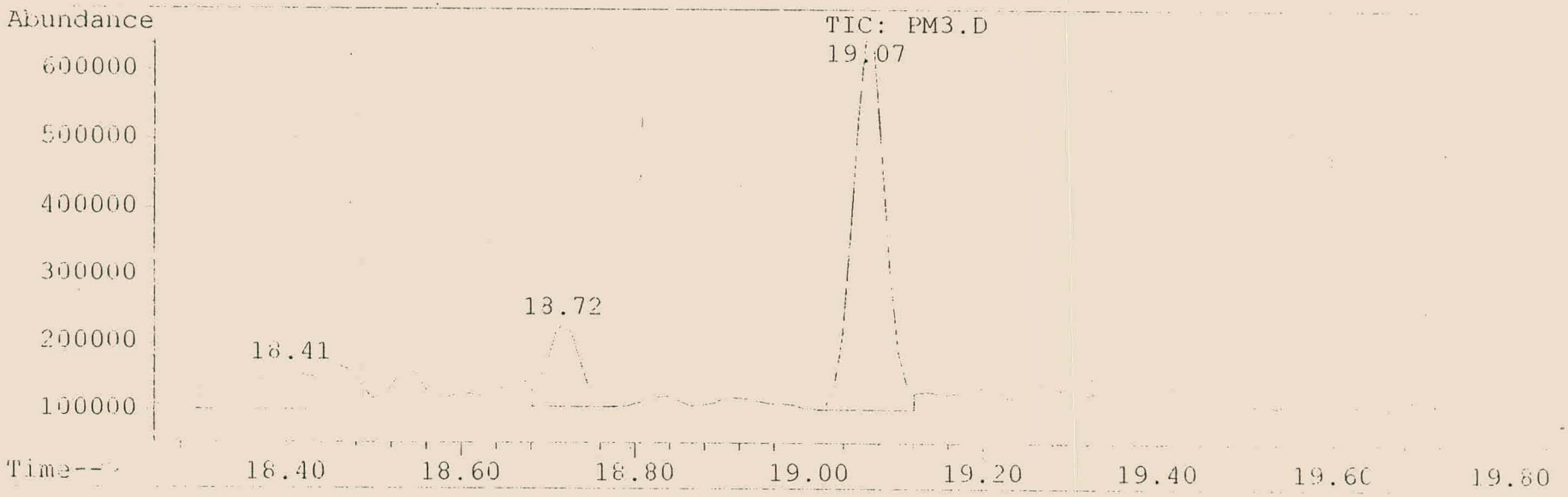
Operator :
Acquired : 3 Jun 99 2:10 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: skoon diesel
Misc Info :
Vial Number: 1

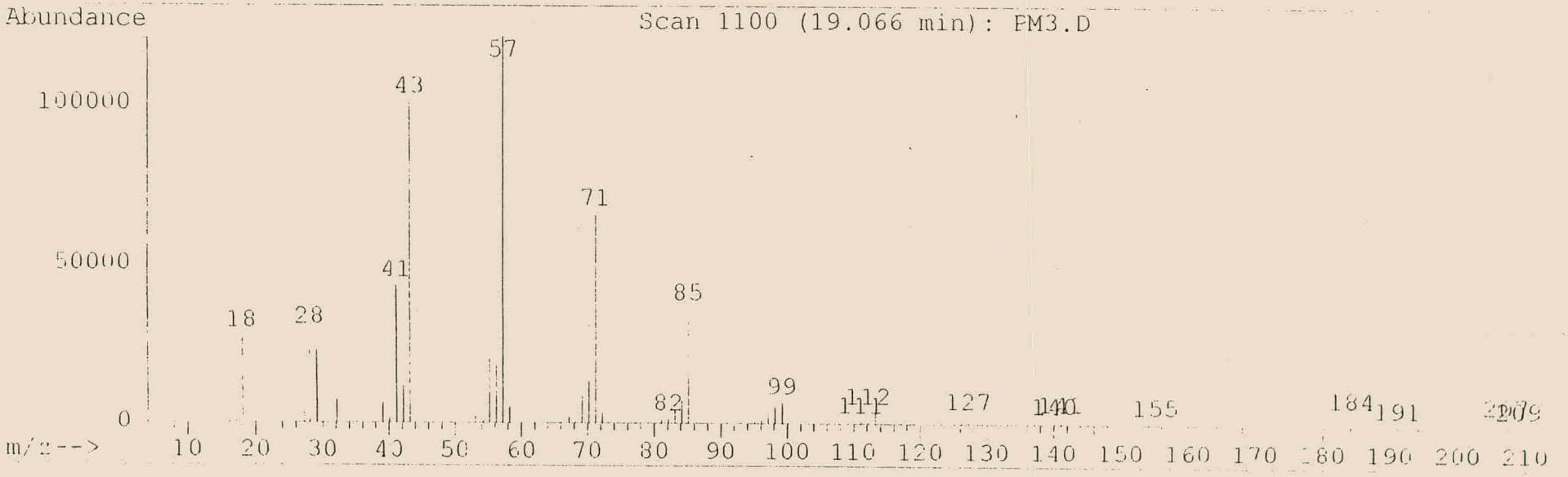




Stellenbosch University https://scholar.sun.ac.za

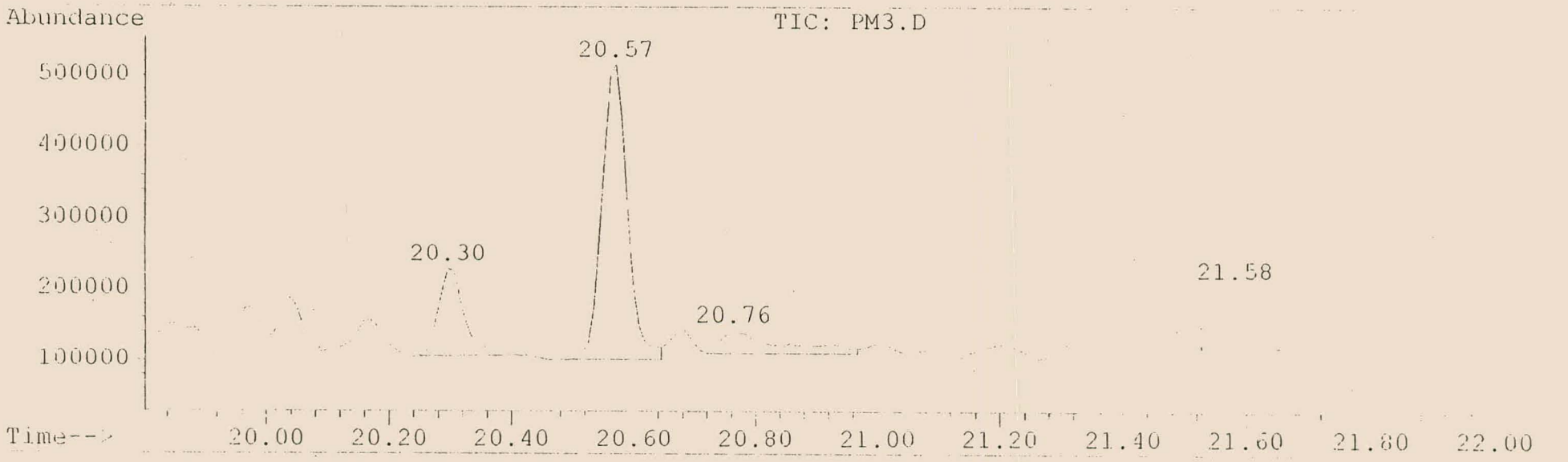
Operator :
Acquired : 3 Jun 99 2:10 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: skoon diesel
Misc Info :
Vial Number: 1

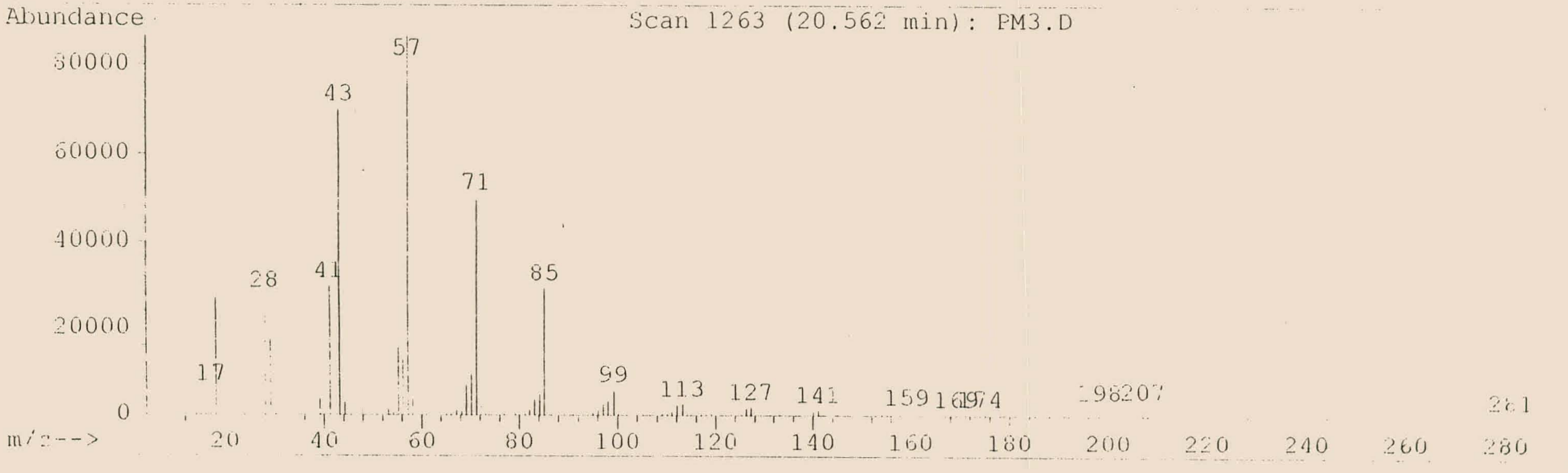




Stellenbosch University https://scholar.sun.ac.za

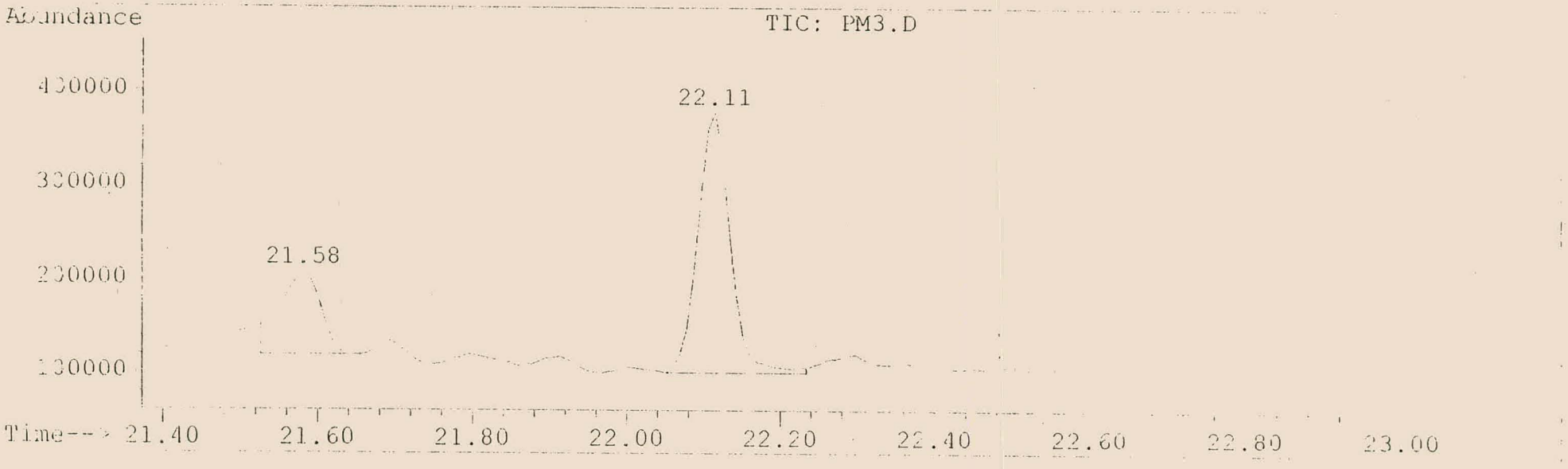
Operator :
Acquired : 3 Jun 99 2:10 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: skoon diesel
Misc Info :
Vial Number: 1

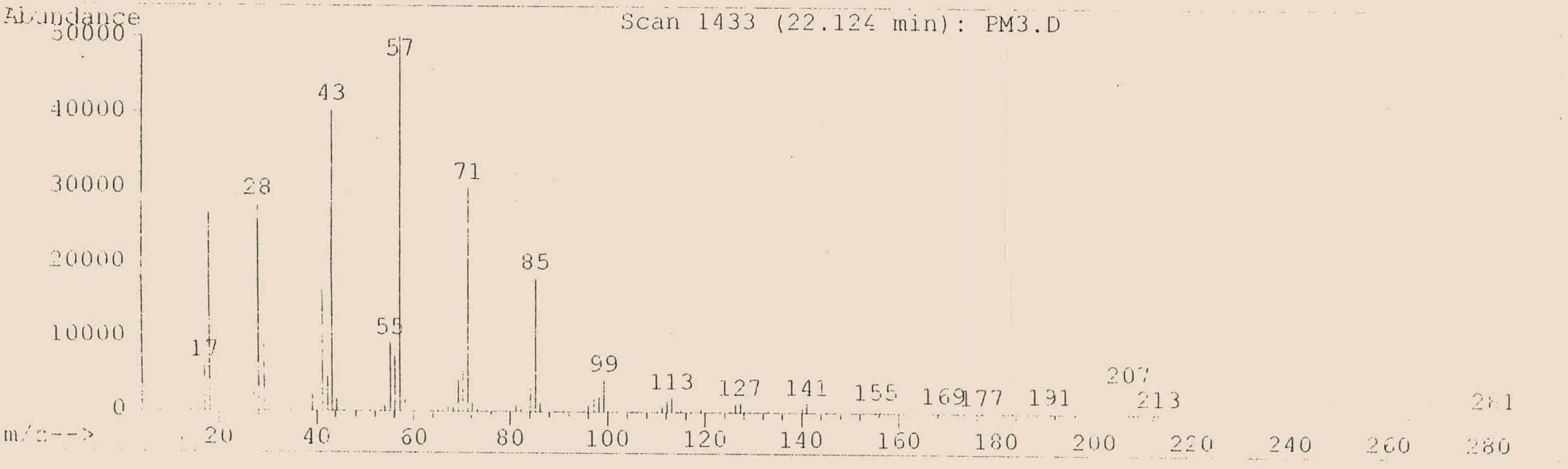




Stellenbosch University https://scholar.sun.ac.za

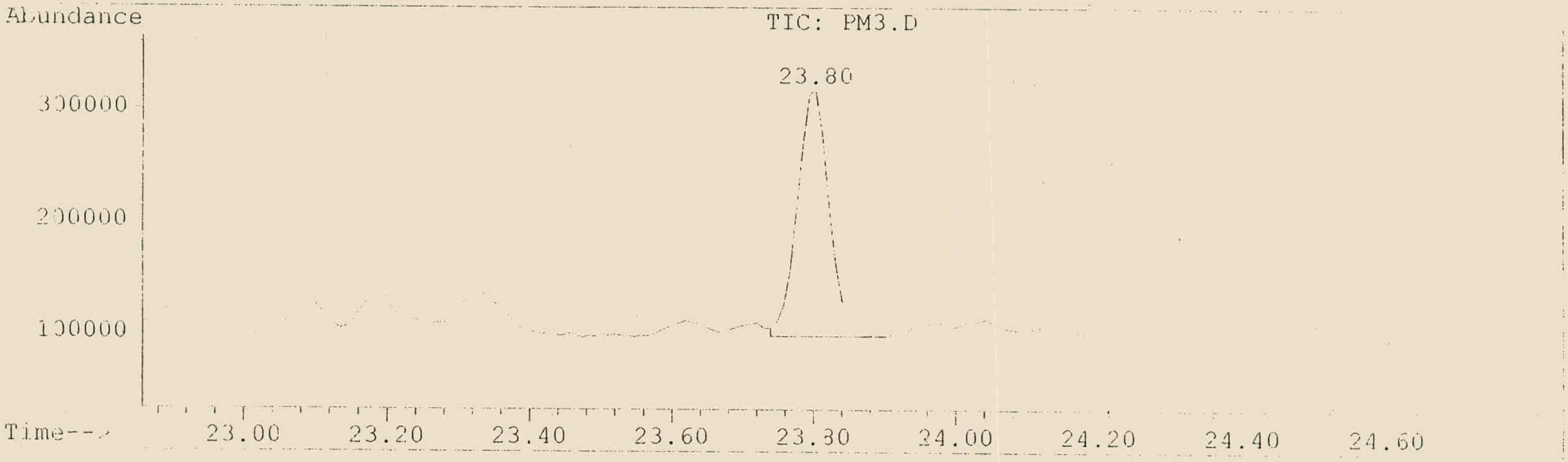
Operator :
Acquired : 3 Jun 99 2:10 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: skoon diesel
Misc Info :
Vial Number: 1

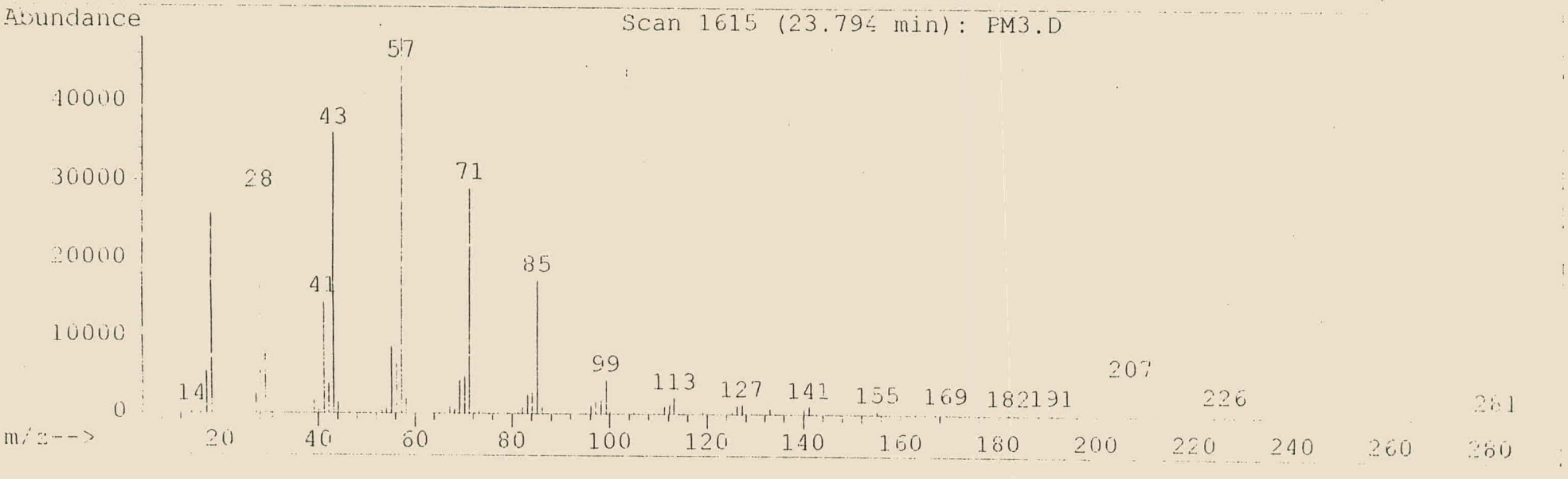




Stellenbosch University https://scholar.sun.ac.za

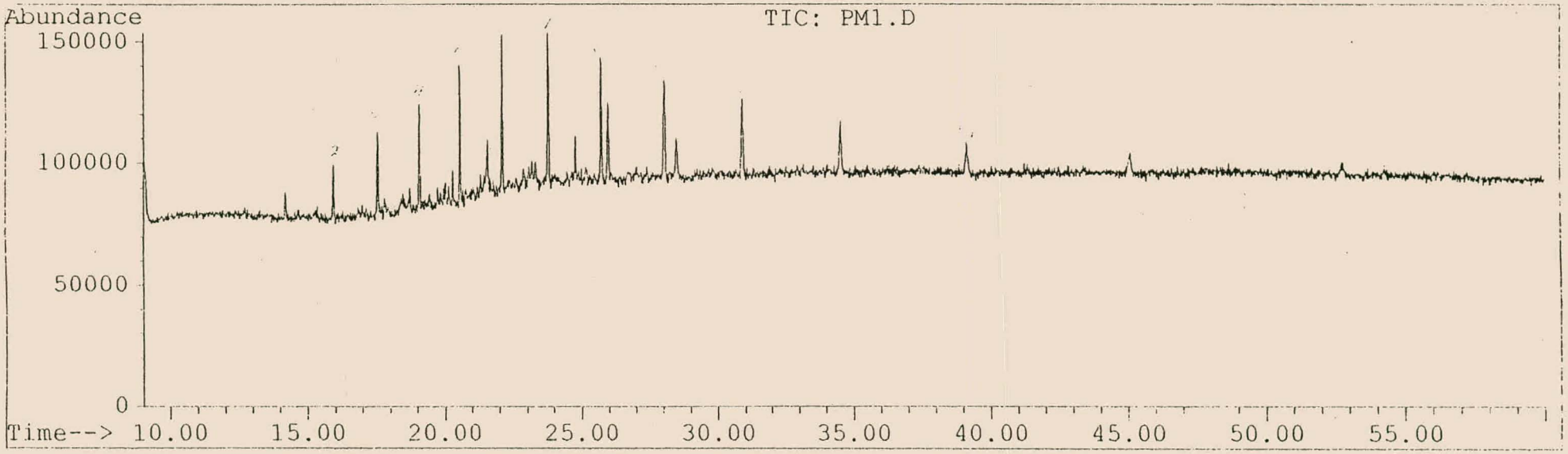
Operator :
Acquired : 3 Jun 99 2:10 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: skoon diesel
Misc Info :
Vial Number: 1





Stellenbosch University https://scholar.sun.ac.za

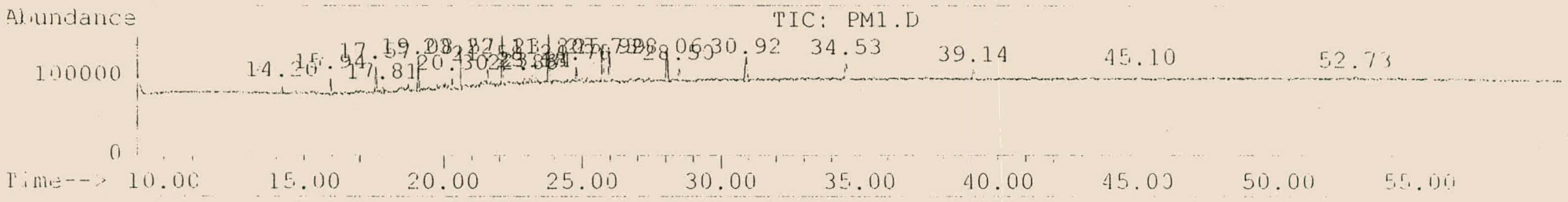
Operator :
Acquired : 21 May 99 1:13 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: jet
Misc Info :
Vial Number: 1



Stellenbosch University https://scholar.sun.ac.za

Area Percent Report -- Sorted by Signal

Information from Data File:
File : C:\HPCHEM\1\DATA\PM1.D
Operator :
Acquired : 21 May 99 1:13 pm using AcqMethod PIETER
Sample Name: jet
Misc Info :
Vial Number: 1
CurrentMeth: C:\HPCHEM\1\METHODS\HANLIE.M



Retention Time	Area	Area %	Ratio %	Type	Width
Total Ion Chromatogram					
14.202	33789	1.645	18.551	rBV	0.109
15.943	69850	3.400	38.349	rVB	0.119
17.566	79219	3.856	43.493	rBV	0.100
17.813	35293	1.718	19.377	rBV	0.110
19.081	121979	5.938	66.969	rBV	0.128
20.305	40439	1.968	22.202	rBV	0.110

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Area Percent Report -- Sorted by Signal

Information from Data File:
File : C:\HPCHEM\1\DATA\PM1.D
Operator :
Acquired : 21 May 99 1:13 pm using AcqMethod PIETER
Sample Name: jet
Misc Info :
Vial Number: 1
CurrentMeth: C:\HPCHEM\1\METHODS\HANLIE.M

Retention Time	Area	Area %	Ratio %	Type	Width
20.570	162280	7.899	89.095	rBV	0.128
21.584	65385	3.183	35.898	rVB	0.110
22.114	177411	8.636	97.403	rVB	0.110
22.882	32990	1.606	18.112	rVB	0.110
23.184	40034	1.949	21.980	rVV	0.128
23.339	31873	1.551	17.499	rVB	0.128
23.796	182142	8.866	100.000	rVB	0.137
24.784	55673	2.710	30.566	rVB	0.110
25.734	169609	8.256	93.119	rVB	0.137
25.990	106169	5.168	58.289	rVB	0.119
28.055	160440	7.810	88.085	rVB	0.146
28.503	81010	3.943	44.476	rVB	0.183
30.924	158005	7.691	86.748	rVB	0.201
34.533	91257	4.442	50.102	rVB	0.146
39.135	70961	3.454	38.959	rVB	0.183
45.098	57602	2.804	31.625	rm	0.265
52.731	30973	1.508	17.005	rm	0.155

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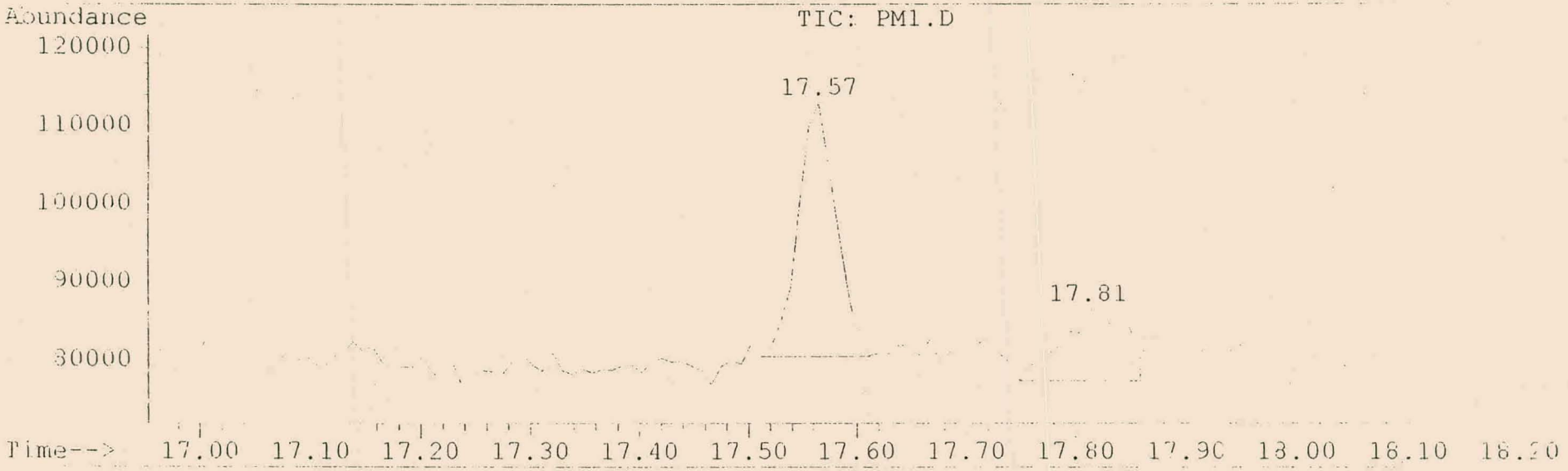
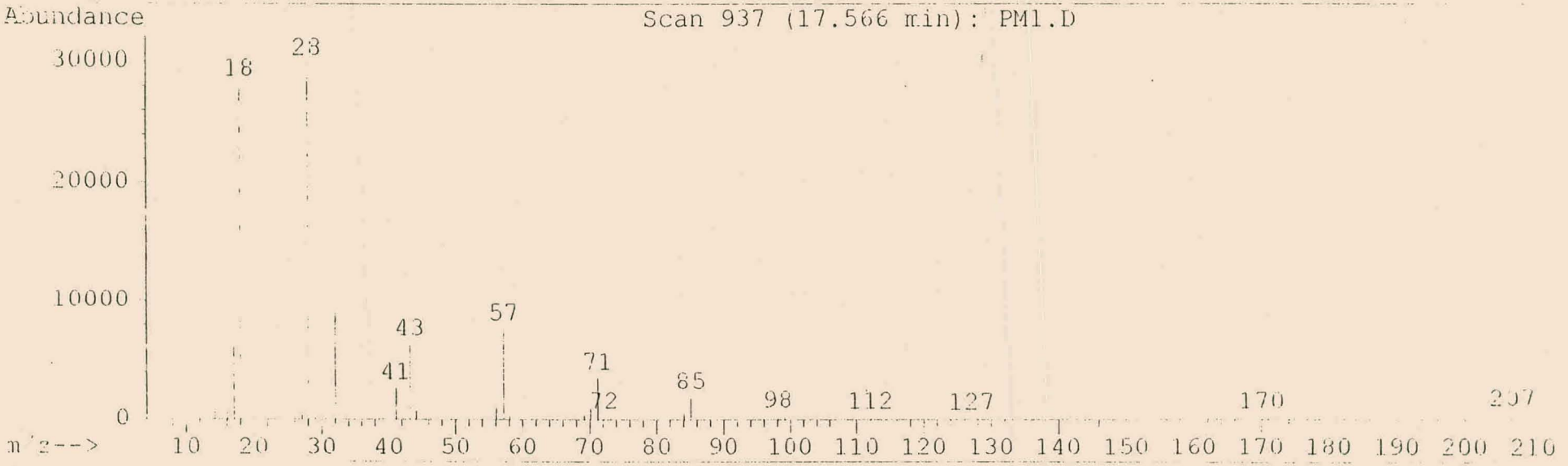
Operator :
Acquired : 21 May 99 1:13 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: jet
Misc Info :
Vial Number: 1





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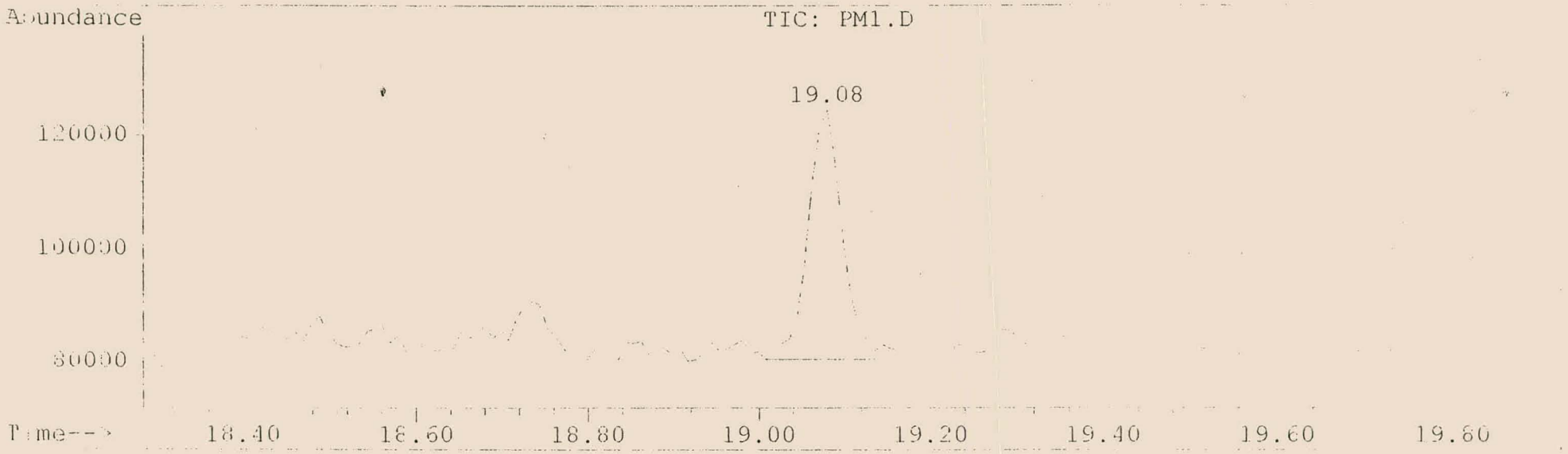
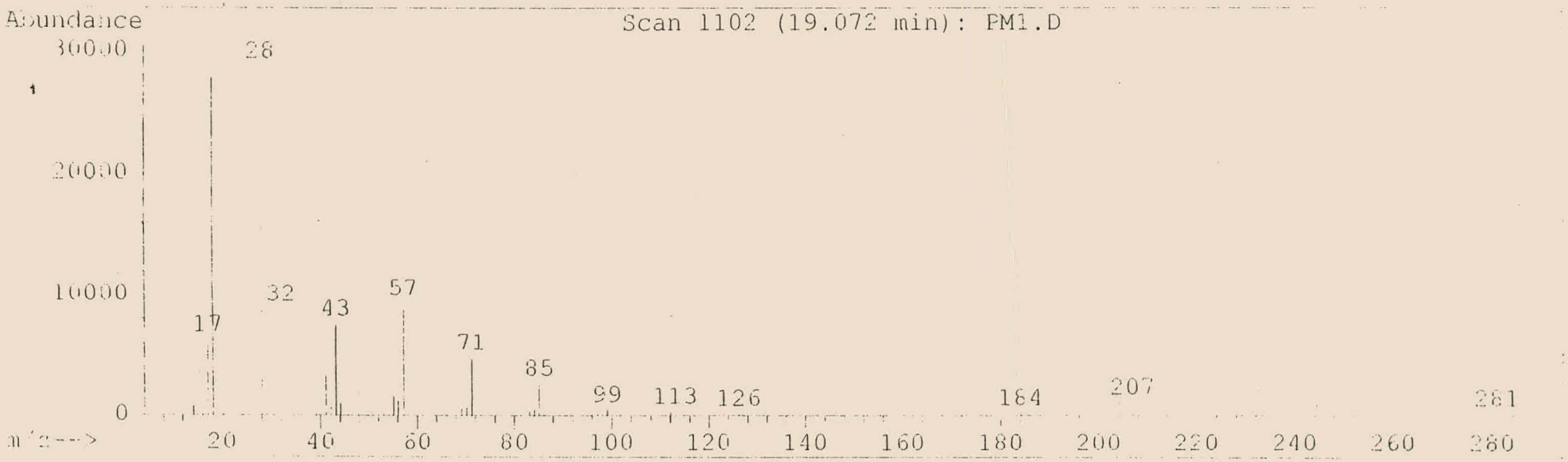
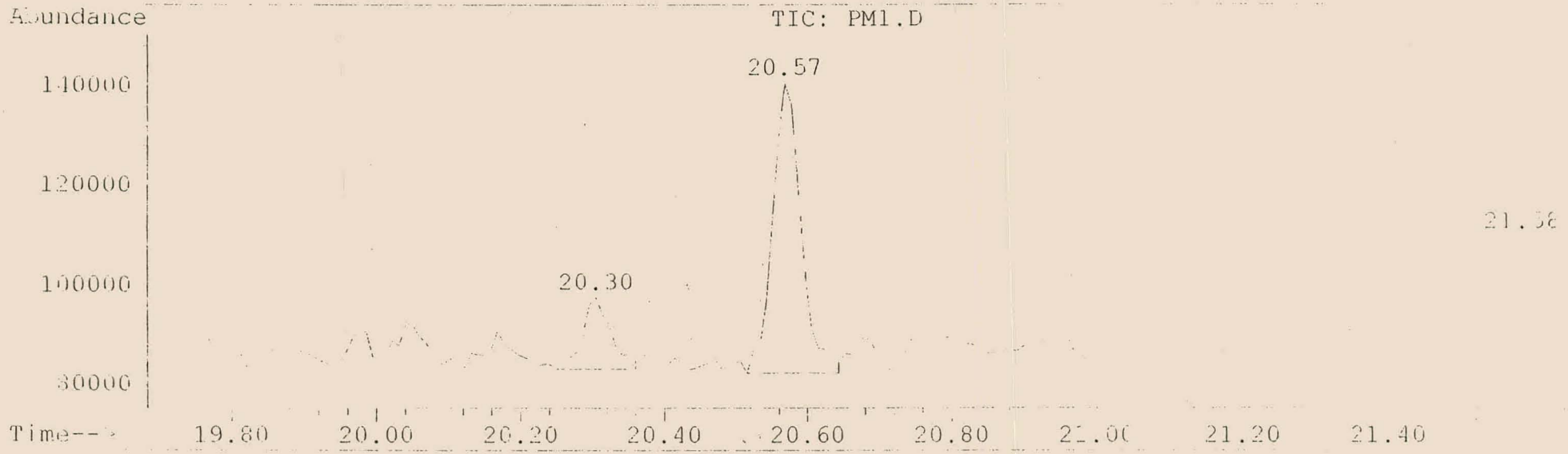
Operator :
Acquired : 21 May 99 1:13 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: jet
Misc Info :
Vial Number: 1

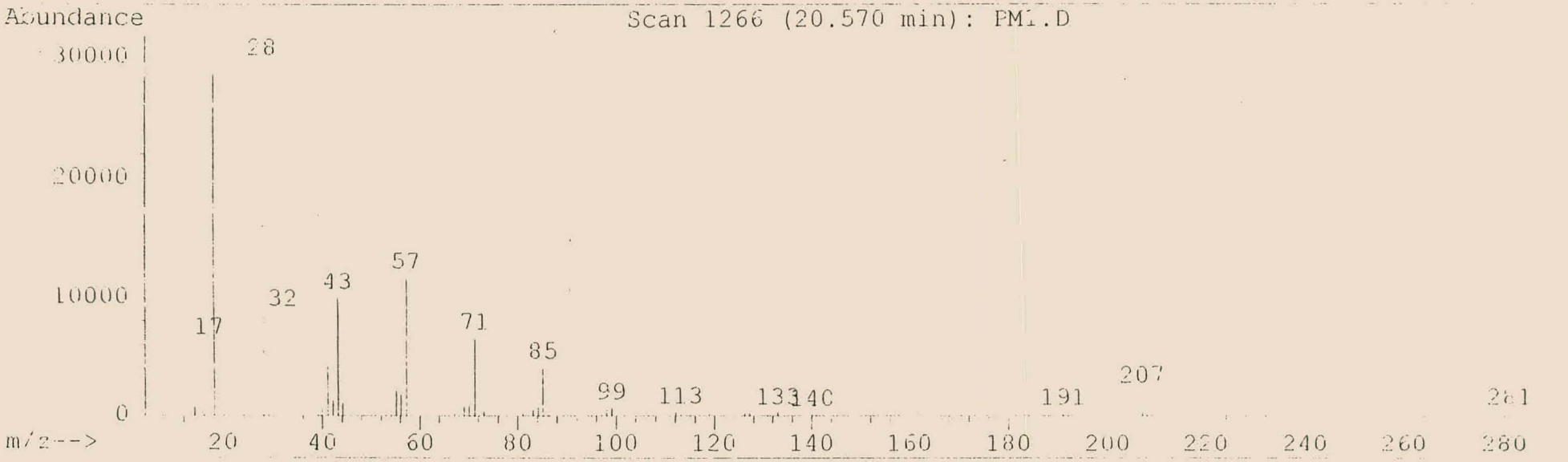




Stellenbosch University https://scholar.sun.ac.za

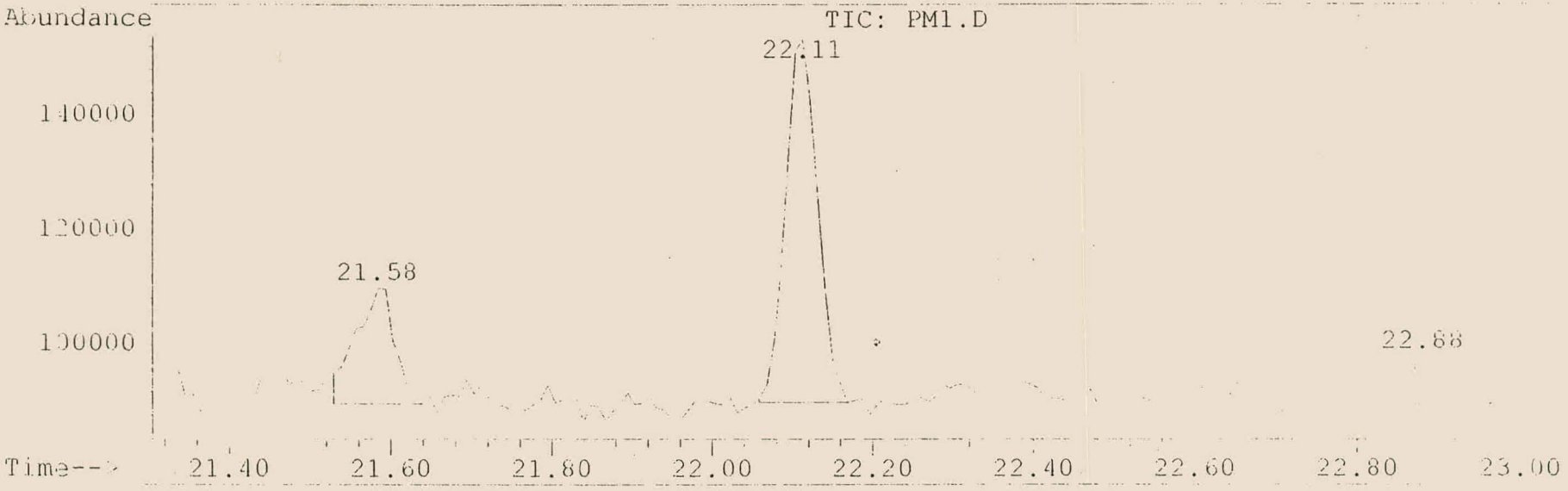
Operator :
Acquired : 21 May 99 1:13 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: jet
Misc Info :
Vial Number: 1

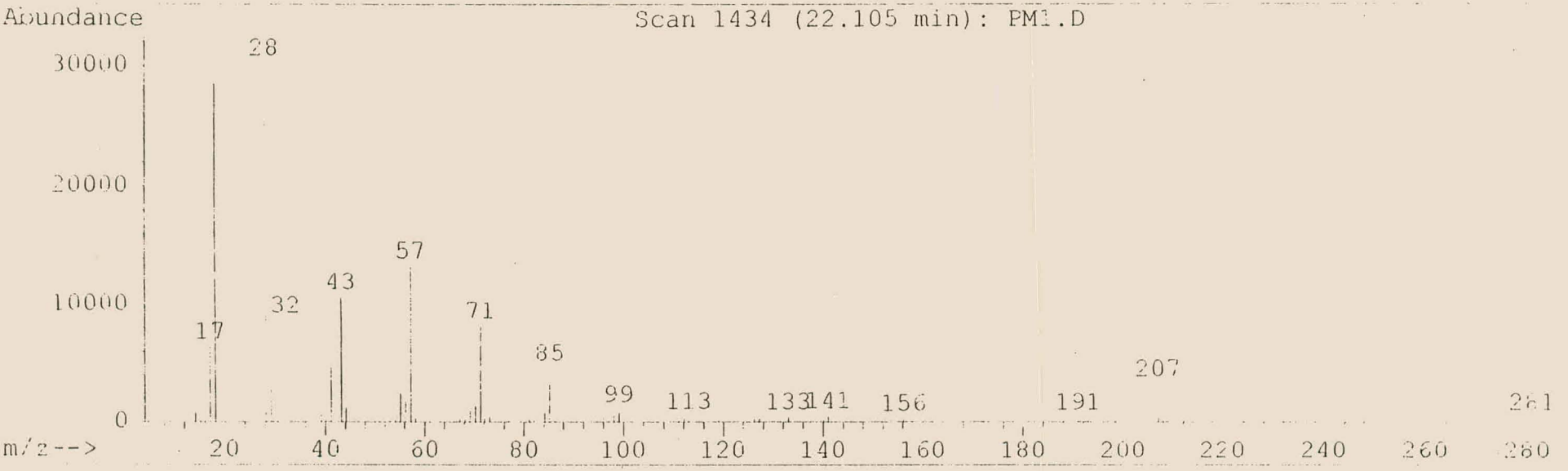




Stellenbosch University https://scholar.sun.ac.za

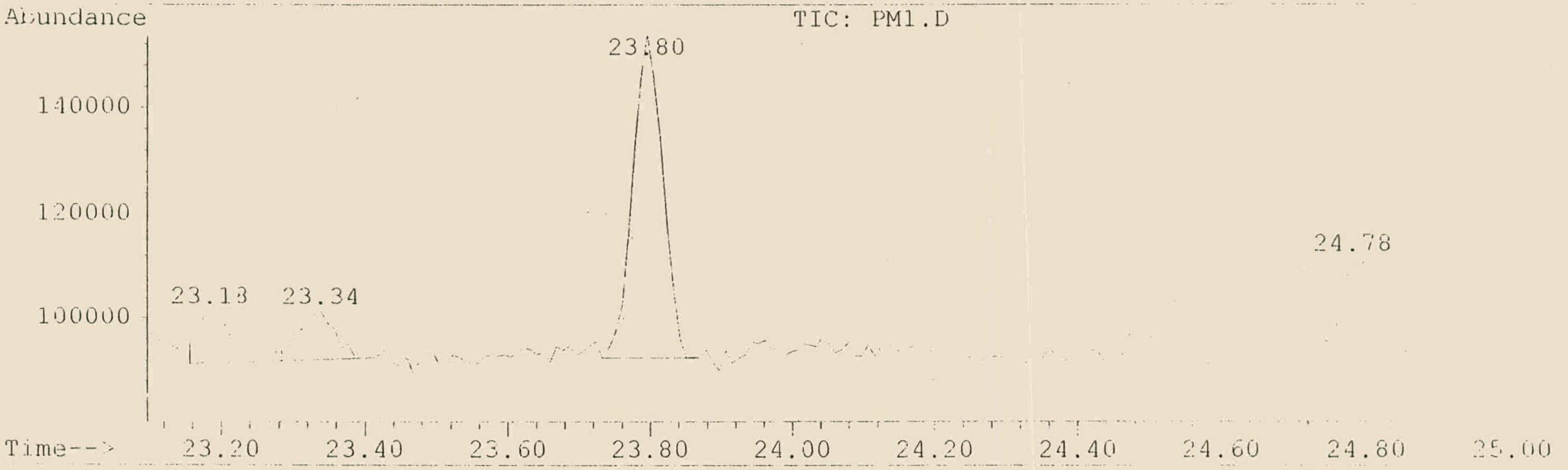
Operator :
Acquired : 21 May 99 1:13 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: jet
Misc Info :
Vial Number: 1

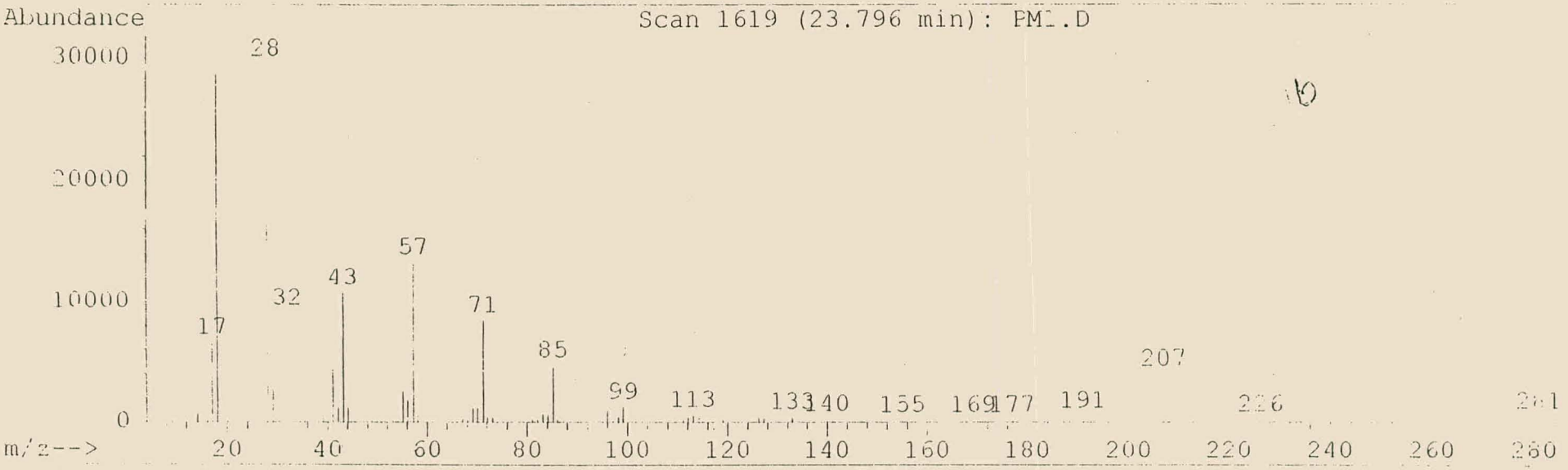




Stellenbosch University https://scholar.sun.ac.za

Operator :
Acquired : 21 May 99 1:13 pm using AcqMethod PIETER
Instrument : GCD
Sample Name: jet
Misc Info :
Vial Number: 1





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APPENDIX B

TYPICAL CALCULATIONS

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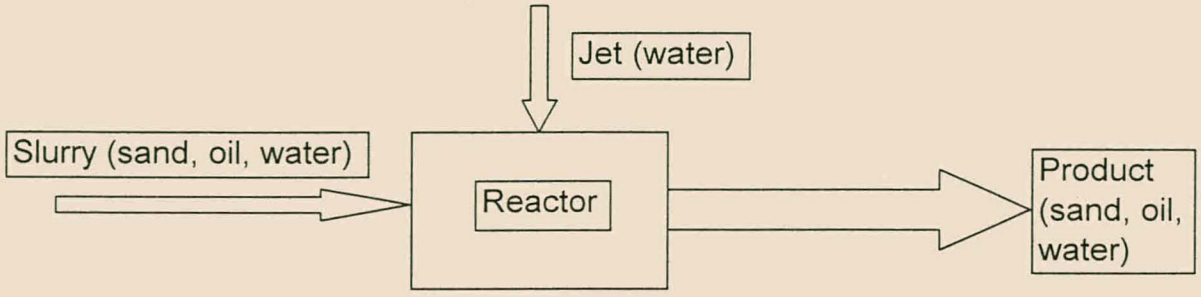
B1: Jet Reactor

Diagram of jet reactor for mass balance purposes:



Run 1a will be used to demonstrate the calculations performed:

Product (Slurry weighed after each run) [kg]	12.2
Sand (Sand in slurry product, weighed after washwater was decanted) [kg]	0.9
Jet Flow (Flowrate measured at jet pressure used) [L/min]	1.8
Jet (Flowrate converted to mass using the density of water and run time) [kg]	3.6
Therefore mass of slurry fed through reactor (From mass balance over reactor) [kg]	8.6
Solids Concentration (of slurry in the reactor to check against that in the feedtank) [%]	10.5

Analysis: 1) 50 g of sand was used and the diesel was extracted into 200 ml of MCL.
2) 25 ml of the extract was left to evaporate and after evaporation of the MCL, the diesel left was weighed.
3) This amount of diesel left was then converted to a concentration of diesel left on the product sand.

Mass of diesel left after evaporation (in 25 ml) [g]	0.0122
Therefore mass of diesel in 200 ml (and so also in the 50 g of sand used) [g]	0.0976
Finally as a concentration [mg/kg or ppm]	1952

B1: SSSA

The sand from these experiments were analysed, and the concentration of diesel on the sand calculated, in exactly the same manner, as with the jet reactor experiments.

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APPENDIX C

DATA SHEETS FOR SAND

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NO. 1 SAND

Grading Analysis

(U.S.) Mesh	Aperature in microns (µm)	% Retained
4	4750	
5	4000	
6	3350	
7	2800	
8	2300	
10	2000	0.4
12	1700	0.2
14	1400	0.4
16	1180	2.2
18	1000	8.3
20	850	18.3
25	710	21.4
30	600	21.1
35	500	19.9
40	425	5.6
45	355	1.9
50	300	0.2
60	250	0.1
70	212	
80	180	
100	150	
120	125	
140	106	
200	75	
-200	-75	

Chemical Analysis

	%
SiO_2	99.75
Al_2O_3	0.07
Fe_2O_3	0.023
TiO_2	0.024
ZrO_2	0.005
CaO	0.003
MgO	traces
L.O.I	0.12

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AFS 35 FOUNDRY SAND

Grading Analysis

(U.S.) Mesh	Aperature in microns (µm)	% Retained
4	4750	
5	4000	
6	3350	
7	2800	
8	2300	
10	2000	
12	1700	
14	1400	
16	1180	
18	1000	
20	850	
25	710	0.1
30	600	
35	500	9.3
40	425	
45	355	48.0
50	300	
60	250	35.0
70	212	3.9
80	180	
100	150	2.1
120	125	
140	106	1.2
200	75	0.4
-200	-75	

Chemical Analysis

	%
SiO_2	99.74
Al_2O_3	0.09
Fe_2O_3	0.018
TiO_2	0.032
ZrO_2	0.005
CaO	0.003
MgO	traces
L.O.I	0.11

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NO. 2 FOUNDRY SAND

Grading Analysis

(U.S.) Mesh	Aperature in microns (µm)	% Retained
4	4750	
5	4000	
6	3350	
7	2800	
8	2300	
10	2000	
12	1700	
14	1400	
16	1180	
18	1000	
20	850	
25	710	
30	600	
35	500	0.3
40	425	
45	355	0.3
50	300	
60	250	1
70	212	2.2
80	180	
100	150	38.7
120	125	
140	106	38.6
200	75	17.7
-200	-75	1.2

Chemical Analysis

	%
SiO_2	99.62
Al_2O_3	0.15
Fe_2O_3	0.034
TiO_2	0.037
ZrO_2	0.009
CaO	0.018
MgO	0.002
L.O.I	0.13

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SILICA 300 MESH

Typical Particle Distribution

Retained on 0.150 mm	0.04%
Retained on 0.075 mm	0.05%
Retained on 0.045 mm	5.50%
Passing 0.045 mm	94.50%
Passing 0.010 mm	42%

Chemical Analysis

	%
SiO_2	99.39
Al_2O_3	0.2
Fe_2O_3	0.13
TiO_2	0.006
CaO	0.02
MgO	0.05
NA_2O	0.03
K_2O	0.01
SO_3	0.009
CR_2O_3	0.4ppm
L.O.I	0.2

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APPENDIX D

SOIL WASHING PROCESS EVALUATION DATA

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Table 4.6
Evaluation of Existing Soil Washing Technologies (1989)

Installation	Rated Throughput	Principal Operations	Particle Reject Size	Fixed or Transportable	Pollutants Treated	Refractory Pollutants	Treatment Fee per Ton	Sludge Disposal Costs per Ton	Capital Costs
Heijmans Milieutechniek b.v. Rosmalen, The Neths.	11 ton/hr	• Particle sizing • Scrubbing with detergents and oxidants • Flocculation • Precipitation	<63 µm	Transportable but fixed	Cyanides Heavy metals PCAs Mineral oil Kerosene	Cl-HCs Aromatics	$73-91 $102 at max 30% <63 µm	$136	New 33 ton/hr plant planned, $4.5 million
HWZ Bodemsan-ering Amersfoort, The Neths.	22 ton/hr	• Particle sizing • Scrubbing with detergents • Flocculation • pH adjustment • Carbon filters	<63 µm	Transportable but fixed	Cyanides Heavy metals aromatics Solvents Cl-HCs	Oily cmpds Br compds	$53 plus $2.50/ton for each % <63 µm, up to 20%	$136	$3 million
Heidemij Realisatie Arnhem, The Neths.	30 ton/hr	• Particle sizing • Froth flotation with cleaning agents • Washing	<38 µm	Fixed	Cyanides Heavy metals PCAs Oils Cl-HCs Pesticides	PAHs PCBs HCH Some heavy metals	$90-155, 2200 tons is min treated	as high as $182	$3 million
Harbauer GmbH Berlin, FRG	16.5-22 ton/hr	• Particle sizing • Low-freq. vibration with extractants • Washing • Water treatment by flotation, air stripping, ion exch. and activated carbon	<15 µm	Fixed	Organics Phenol PAH Org-Cl cmpds PCBs	Heavy metals	$136 (excludes residue disposal)	Sludge stored to date	$4.5-6 million
TBSG Industrievertretungen GmbH- Oil CREP System Bremen, FRG	44 gpm New 88 gpm plan planned	• Particle sizing • Washing with Oil CREP 1 • Solid/liquid separation	<100 µm	Mobile	Extractables HCs PAHs Extr. Hal-org.	PCBs Fl-HCs Cyanides Heavy metals	$82-109 excluding disposal of residues, 3920 cu yds min treated	$6K/day sludge treatment	Not known at this time

Source: US EPA 1988

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Table 17-3. Summary of Performance Data and Technology Status - Part I

Proprietary Vendor Process/EPA	Highest Scale of Operation	Year Operation Began	Range of Particle Size Treated	Contaminants Extracted from Soil	Extraction Agent(s)
U.S. Processes					
(1) Soil Cleaning Company of America [5; 15, p. 2]	Full-scale 15 tons/hr	1988	Bulk soil	Oil and grease	Hot water with surfactant
(2)[a] Biotrol Soil Treatment System (BSTS) [4, p. 6; 12]	Pilot-scale 500 lbs/hr	Fall, 1987	Above clay size and below 0.5 in. Some cleaning of fine particles in bio-reactor	Organics - pentachlorophenol, creosote, naphthalene, pyrene, fluorene, etc.	Proprietary conditioning chemicals
(3) EPA's Mobile Countercurrent Extractor [9; 5, p. 5]	Pilot-scale 4.1 tons/hr	Modified with drum washer and shakedown - 1982 Full-scale - 1986	2-25 mm in drum washer <2 mm in four-stage extractor	Soluble organics (phenol, etc.) Heavy metals (Pb, etc.)	Various solvents, additives, surfactants, redox acids and bases. Chelating agent (EDTA)
(4)[a] EPA's First Generation Pilot Drum Screen Washer [10, p. 8]	Pilot-scale	1988	Oversize (>2 mm) removed prior to treatment	Petroleum hydrocarbons	Biodegradable surfactant (aqueous slurry)
(5)[a] MTA Remedial Resources (MTARRI) Froth Flotation [11; 15, p. 2]	Bench-scale	N/A	Oversize removed prior to treatment	Organics (oil) Heavy metals (inorganics) removed using countercurrent decantation with leaching	Surfactants and alkaline chemicals added upstream of froth flotation cells. Acid for leaching.
Non-U.S. Processes					
(6) Ecotechniek BV [2, p. 17]	Commercial 100 ton/hr mass	1982	Sandy soil	Crude oil	None. Water-sand slurry heated to 90°C max. with steam.
(7) Bodemsanering Nederland BV (BSN) [2, p. 17]	Commercial 20 ton/hr	1982	>100 mm removed No more than 20% <63 µm Sludge <30 µm not cleaned	Oil from sandy soil	None. Uses high pressure water jet for soils washing.

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(8) Harbauer [2, p. 20; 7, p. 5]	*Commercial 15–20 ton/hr*	Lab - 1985 Commercial - 1986 With fines removal - 1987	15 µm - 5 mm Pre-treatment: coarse screens, electromagnet blade washer	Mostly organics Limited heavy metals removal experience	Hydraulically produced oscillation/vibration Surfactants Acid/base
(9) HWZ Bodemsanering BV [2, p. 17]	Commercial 20–25 ton/hr	1984	<10 mm and >63 µm	Cyanide, chlorinated HC, some heavy metals, PNA	Sodium hydroxide to adjust pH Surfactants
(10) Heijman Melieutechniek BV [2, p. 17; 7, p. 6]	Pilot-scale 10–15 ton/hr	1985	<10 mm and no more than 30% <63 µm	Cyanide, heavy metals, mineral oil (water immiscible hydrocarbons)	Proprietary extraction agents. Hydrogen peroxide (H_2O_2) added to react with extracted CN to form CO_2 and NH_3
(11) Heidemij Froth Flotation [7, p. 8]	Full-scale	N/A	<4 mm and no more than 20% <50 µm	Cyanide, heavy metals, chlorinated HCs, oil, toluene, benzene, pesticides, etc.	Proprietary surfactants and other proprietary chemicals
(12) EWH Alsen-Breitenburg Dekomat System [2, p. 20]	Pilot-scale 8–10 cu. m/hr	N/A	<80 mm Clays treated offsite	Oil from sandy soil	Proprietary
(13) TBSG Industrieveitietungen Oil Crep I System [7, p. 7]	Pilot-scale 1986	1986	Sand <50 mm Particles <100 µm treated offsite	Hydrocarbon and oil	Proprietary combination of surfactants, solvents, and aromatic hydrocarbons
(14) Klockner Umweltechnik Jet-Modified BSN [2, p. 20]	Pilot-scale	N/A	No more than 20% <63 µm	Aliphatics and aromatics with densities < water, volatile organics, some other hydrocarbons	None. Soil blasted with a water jet (at 5,075 psi)

[a] Process evaluated or used for site cleanup by the EPA. N/A = Not Available.

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Table 17-3. Summary of Performance Data and Technology Status - Part II

Proprietary Vendor Process/EPA	By-Product Wastes Generated	Extraction Equipment	Efficiency of Contaminant Removal			Additional Process Comments
			Contaminant	% Removal	Residual ppm	
U.S. Processes						
(1) Soil Cleaning of America	Wet oil	Screw conveyors	Oil and grease	50-83	250-600	Three screw conveyors operated in series, hot water with surfactant injected into each stage. Final soil rinse on a fourth screw conveyor.
(2)[a] Biotrol Soil Treatment System (BSTS)	Oil and grease Sludge from biological treatment	Agitated conditioning tank Froth flotation Slurry bioreactor	For the case presented: 90-95% for pentachlorophenol; to residuals <115 ppm. 85-95% for most other organics; to residuals <1 ppm.			Dewatered clays and organics to be treated offsite by incineration, solidification, etc. Washed soil was approx. 78% of feed. Therefore, significant volume reduction was achieved.
(3) EPA's Mobile Counter-Current Extractor	Clay fraction Recovered organics (extractor skimmings) Spent carbon (oversize)	Drum screen Water knife Soil scrubber 4-stage counter-current chemical extractor	Phenol As_2O_3	90 from in. soil 80 from or. soil 50-80	1 96 0.5-1.3	Clay fraction treated elsewhere.
(4)[a] EPA's First Generation Pilot Drum Screen Washer (PDSW)	Sludge Flocculated fines	Drum screen washer	Oil and grease Soil size fraction: 0.25-2 <0.25	99 90	<5 2400	Process removal efficiency increases if extracting medium is heated. Install wet classifiers beneath the PDSW to remove waste-water from treated soil. Auger classifiers are required to discharge particles effectively.

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(5)[a] MTA Remedial Resources (MTARRI) Froth Flotation	*Flocculation froth*	Reagent blend tank Flotation cells Counter-current decantation	Volatile organics Semivolatile organics Most fuel products	98-99+ 98-99+ 98-99+	<50 <250 <2200	Flotation cells linked by underflow weir gates. Induced air blown down a center shaft in each cell. Continuous flow operation. Froth contains 5-10% wt% of feed soil.
Non-U.S. Processes						
(6) Ecotechniek BV	Wet oil	Jacketed, agitated tank	About 90% 20,000 ppm residual oil			Effectiveness of process dependent on soil particle size and type of oil to be separated.
(7) Bodemsanering Nederland BV (BSN)	Oil/organics recovered from wastewater fines	Water jet	Selected results: Aromatics PNAs Crude oil	 >81 85 97	 >45 15 2300	No comments.
(8) Harbauer of America	Carbon which may contain contaminants	Conditioning tank Low frequency vibration unit	Organic-Cl Tot. organics Tot. phenol PAH PCB	96 86-94 86-90 84-88	ND 159-201 7-22.5 91.4-97.5 0.5-1.3	Vibrating screw conveyor used. Cleaned soil separated from extractant liquor in stages; coarse soil by sedimentation, medium fraction in hydroclone, fines (15-20 μm) by vacuum filter press.
(9) HWZ Bodemsanering BV	Fines Sludge containing iron cyanide Large particles—carbon, wood, grass	Scrubber (for caustic addition) Upflow classifier	CN PNAs Chlorinated-HC Heavy metals	95 98 98 75	5-15 15-20 <1 75-125	When the fines fraction (<63 μm) is grater than 20%, the process is not economical. HWZ has had some problems in extracting PNAs and oily material.

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Table 17-3. Continued

Proprietary Vendor Process/EPA	By-Product Wastes Generated	Extraction Equipment	Efficiency of Contaminant Removal			Additional Process Comments
(10) Heijman Milieutechniek BV	Flocculated fines sludge Oil (if any) and silt	Mix tank followed by soils fraction equipment—hydroclones, sieves, tilt plate separators	Cyanide Heavy metal cations	93–99 approx. 70	<15 <200	Process works best on sandy soils with a minimum of humus-like compounds. Because no sand or charcoal filters are employed by Heijman, the system does not remove contaminants such as chlorinated hydrocarbons.
(11) Heidemij Froth Flotation	Contaminated float	Conditioning tank Froth flotation tanks	Cyanide Heavy metals Chlorinated-HC Oil	>95 >90 avg >99 >99	5 >150 0.5 20	Process has broad application for removing hazardous materials from soil. Most experience has been on a laboratory scale.
(12) EWH Alsen-Breitenburg Dekomat System	Recovered oil Flocculated fines (sludge)	High-shear stirred tank	About 95% oil removed			Cleaned soil from high shear stirred tank is separated into fractions using vibrating screens, screw classifiers, hydroclones, and sedimentation tanks.
(13) TBSG Industrieveitiet-Ungen Oil Crep I System	Oil phase containing Oil Crep I	Screw mixer followed by a rotating separation drum for oil recovery	>95% removal of hydrocarbons has been achieved. Results are influenced by other contaminants present.			Oil Crep system was used successfully in Flansburg, FRG (in 1986) to remove PCBs, PAHs, and other hydrocarbons.
(14) Klockner Umweltechnik High Pressure Water Jet-Modified BSN	Oil/organics recovered from wastewater fines Sludge	Water jet - circular nozzle arrangement	Selected results: HC Chlorinated-HC Aromatics PAHs Phenol	 96.3 >75 99.8 95.4 >99.8	 82.05 <0.01 <0.02 15.48 <0.01	No comments

[a] Process evaluated or used for site cleanup by the EPA.
N/A = Not Available.